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Alkyl Toluene Sulfonate Detergents
Attorney D#81,568

This Application claims priority to: US Provisional patent application 60/227,795 filed August 25, 2000 and U. S. Provisional Application No. 60/178,823 filed 01/28/00, which are both currently still pending; 09/174,891 filed 10/19/98; co-pending application serial number 08/879,745, filed June 20, 1997, (which is a divisional of serial number 08/598,695, filed February 8, 1996, now U. S. Patent 5,770,782); and is a continuation-in-part application of co-pending application serial numbers: 09/616,568 filed 7/14/00; 09/559,841 filed April 26, 2000, the contents of all which are expressly incorporated herein by reference.

BACKGROUND OF THE INVENTION

This invention relates generally to detergent compositions and cleaning compositions having enhanced detergency and cleaning capabilities. It relates more particularly to detergent and cleaning compositions containing the 2-tolyl isomer of linear alkyltoluene sulfonates in concentrations higher than were previously available in the prior art, owing to the discovery of the revolutionary catalyst and process for producing such isomers in high concentration, as detailed herein. According to a preferred form of the invention, an alkylated benzene, such as toluene or ethylbenzene, are utilized as an aromatic compound that is further alkylated and sulfonated to provide a surfactant useful in detergent formulations.

Chemical compounds useful for removing grease, oils, dirt and other foreign matter from various surfaces and objects have been known for some time, including the simple soaps which are manufactured by the saponification of oils (including

animal fats and vegetable oils). Saponification is essentially a process whereby aqueous alkali metal hydroxide is mixed with an ester (such as an animal fat or vegetable oil) to cause de-esterification of the ester with the formation of the alkali salt(s) of the carboxylic acid(s) from which the ester was derived, which salt(s) are typically very soluble in aqueous media. Importantly, the anion portions of such alkali salts of the carboxylic acid(s) include as part of their molecular structure a hydrophilic portion, i.e., the carboxylate function, which is highly attracted to water molecules. Such salts also include a hydrophobic portion as part of their molecular structure, which is typically a hydrocarbon-based portion containing between about 12 and 22 carbon atoms per molecule. Such salts are commonly referred to by those skilled in the art as "salts of fatty acids", and by laypersons as "soap". Aqueous solutions of salts of fatty acids are very effective at causing grease, oils, and other normally water-insoluble materials to become soluble and thus capable of being rinsed away, thus leaving behind a clean substrate which may typically comprise a tabletop, countertop, article of glassware or dinnerware, flatware, clothing, architecture, motor vehicle, human skin, human hair, etc.

While the industries for the production of such soaps from fats and oils are well-established, saponification chemists and other workers have continuously sought improved chemistry for rendering materials which are not normally soluble in aqueous media to become soluble therein. Towards this end, a wide variety of materials have been identified by those skilled in the art, with the common denominator of such materials being that the materials all contain a hydrophobic portion and a hydrophilic portion in their molecular structures.

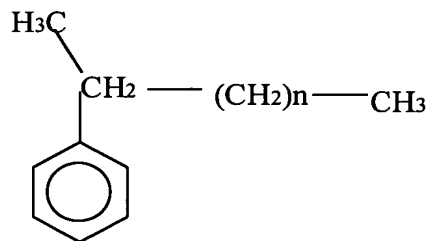
One family of materials that have been identified as suitable soap substitutes are the linear alkylbenzene sulfonates ("LAB sulfonates"). The LAB sulfonates in general are exemplified as comprising a benzene ring structure having a hydrocarbyl substituent (or "alkyl substituent") and a sulfonate group bonded to the ring in the para position with respect to one another. The length of the hydrocarbon chain of the alkyl substituent on the ring is selected to provide a high level of detergency characteristics while the linearity of the hydrocarbon chain enhances the biodegradability characteristics of the LAB sulfonate. The hydrocarbyl substituent may typically contain 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 carbon atoms (the "detergent range") in a substantially linear arrangement, and may be attached to the benzene ring by means of a conventional Friedel-Crafts alkylation process using a corresponding olefin and employing a Lewis acid catalyst such as aluminum chloride and conditions known to those skilled in the art as useful for such alkylations. Various alkylation processes useful for production of alkylbenzenes are described in US Patent numbers 3,342,888; 3,478,118; 3,631,123; 4,072,730; 4,301,316; 4,301,317; 4,467,128; 4,503,277; 4,783,567; 4,891,466; 4,962,256; 5,012,021; 5,196,574; 5,302,732; 5,344,997; and 5,574,198, as well as European patent application 353813 and Russian patent 739,046, the entire contents of which are incorporated herein by reference thereto.

Once a hydrocarbyl radical has been appended to a benzene ring in accordance with the foregoing, the resulting linear alkylbenzene must subsequently be sulfonated in order to produce a finished detergent material that is capable of solubilizing grease, oils, dirt, and the like from various substrates, such as dishes, motorized vehicles, hard surfaces, architecture, and fabrics, to name but a few. Sulfonation is a known chemical process whose reactants and conditions are known to those skilled in the

chemical arts. Through the process of sulfonation, a sulfonate group is caused to become chemically bonded to a carbon atom in the benzene ring structure of the linear alkylbenzene, thus providing the molecule as a whole with a hydrophilic sulfonate group in addition to the hydrophobic hydrocarbyl portion.

It is known that during the course of mono-alkylation of the benzene ring to introduce a hydrocarbon tail into the molecular structure, several structural isomers are possible in which the benzene ring is attached to various points along the hydrocarbon chain used. It is generally believed that steric effects of the mono-olefin employed play a role in the distribution of isomers in the mono-alkylated product, in addition to the catalyst characteristics and reaction conditions. Thus, it is possible for a single benzene ring to become attached to, say, the 2, 3, 4, or 5 positions in a 10 carbon atom linear mono-olefin, with a different alkylbenzene isomer being produced in each such case. Sulfonation of such different materials results in as many different alkylbenzene sulfonates, each of which have different solubilization capabilities with respect to various oils, grease, and dirt, etc.

The sulfonates of the 2-phenyl alkyl isomers are regarded by those skilled in the art as being very highly desirable materials, as sulfonated linear alkylbenzene detergent materials made from sulfonation of the 2-phenyl alkyl materials have superior cleaning and detergency powers with respect to the sulfonation products of other isomers produced during the alkylation. This is believed to be due in part to the greater degree of separation of the hydrophobic and hydrophilic portions of the molecule in the 2-phenyl isomer than in the other isomers present. The most desired 2-phenyl alkyl isomer products may be represented structurally, in the case of the alkylbenzenes, as:



which in a preferred embodiment has n equal to any integer selected from the group consisting of: 5, 6, 7, 8, 9, 10, 11, and 12. Since the Friedel-Crafts type alkylation employed to produce 2-phenyl alkyl isomers according to the invention may often utilize a mixture of olefins in the detergent range (C_8 to C_{15}), a distribution of various alkylbenzenes results from such alkylation.

These same considerations as above relating to linear alkylbenzenes are also applicable to the linear alkyltoluenes of this invention. The present invention is therefore in one broad respect concerned with the use of sulfonated 2-toluy alkyltoluenes derived from the alkylation of toluene, preferably using olefins having a carbon number distribution in the detergent range, in detergent formulations.

In the case of benzene alkylation using a detergent range olefin, a 2-phenyl alkylbenzene is but one possible structural isomer resulting from the alkylation of benzene with an olefin, and a mixture of 2-phenyl alkylbenzenes results from the alkylation of benzene using as reactants a feed which includes a mixture of olefins in the detergent range. This may be due to resonance stabilization which permits effective movement of the double bond in an activated olefin/Lewis acid complex. Generally speaking, the collection of all isomeric products produced from the alkylation of benzene with a mixture of olefins in the detergent range is commonly

referred to by those of ordinary skill in the art as "linear alkylbenzenes", or "LAB's". Frequently, those skilled in the art use "linear alkylbenzenes" or "LAB's" interchangeably with their sulfonates. It is common for people to say LAB's when they are actually referring to sulfonated LAB's useful as detergents. These same considerations apply to linear alkyltoluenes as well, and linear alkyltoluenes may be referred to as "LAT's".

Typically, LAB's are manufactured commercially using classic Friedal-Crafts chemistry, employing catalysts such as aluminum chloride, or using strong acid catalysts such as hydrogen fluoride, for example, to alkylate benzene with olefins. While such methods produce high conversions, the selectivity to the 2-phenyl isomer in such reactions as known in the prior art is low, generally being about 30% or less. LAB's with a high percentage of the 2-phenyl isomer are highly desired because such compounds when sulfonated have long "tails" which provide enhanced solubility and detergent properties.

While the alkylation of benzene to provide alkylbenzenes that are further sulfonated to afford surfactants has served the industry well for decades, there are disadvantages associated with the use of benzene. For example, benzene is a toxic material which requires specialized equipment for its safe handling, and which is traded under stringent regulation by various governmental bodies. Thus, mere handling and health aspects have provided a motivation for chemists to seek alternative surfactants which are effective, but are not based on benzene.

Further, the price of benzene is generally higher than other aromatic compounds which may be suitable candidates from which surfactants may ultimately be derived, such as toluene and ethylbenzene.

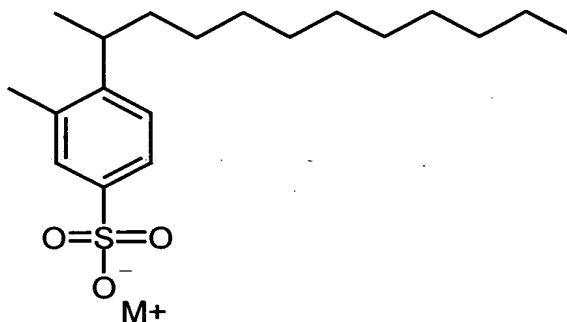
One of the most important aspects of a surfactant that is intended to be utilized in aqueous solution is its solubility. Formulations need good solubility in order to perform well. As mentioned, surfactant molecules generally comprise a hydrophobic portion and a hydrophilic portion. As the hydrophobic group increases in molecular weight (the hydrophilic group being held the same), the surfactant becomes less soluble in water. Similarly, for the same hydrophobic group, the surfactant becomes more water soluble as the hydrophilic group becomes more water soluble.

Surfactants exhibit behavioral characteristics which differ from those exhibited by most other organic molecules. The solubility of most chemical compounds in water increases as the temperature of the water is increased. The solubility of ionic surfactants increases dramatically above a certain temperature known as the Krafft point. When the solubility of an ionic surfactant is plotted against temperature, a complex graph results. The solubility slowly increases as the temperature rises up to the Krafft temperature, after which there is seen a very rapid rise in solubility with only moderate increases in temperature, and it is at the Krafft temperature at which micelles are formed. Below the Krafft temperature, solubility is limited as no micelles are formed. Thus, a surfactant having a Krafft temperature that is above the temperature at which the surfactant is intended to be used will not have sufficient solubility at the use temperature to be effective as a surfactant.

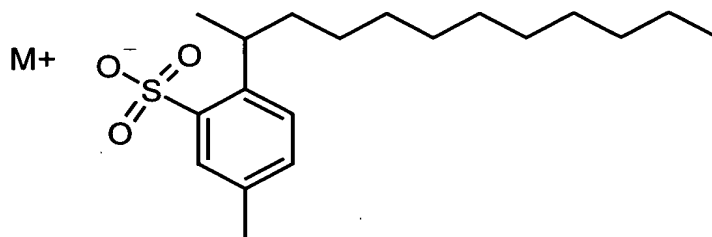
Thus, providing a surfactant material having an sufficiently high Krafft temperature to enable its use at ordinary temperatures; and which surfactant is not benzene-derived, represents a very desirable goal. To provide such a material having higher 2-phenyl isomer content over that available in the art so as to increase its detergency characteristics would be a huge step forward in the art of detergents.

SUMMARY OF THE INVENTION

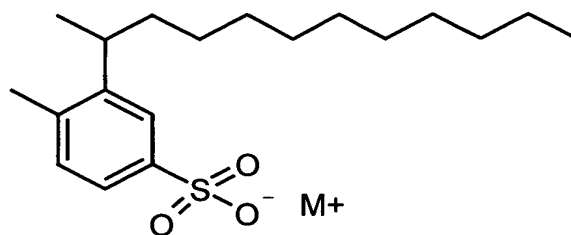
According to the present invention, linear alkyltoluene sulfonate surfactants are provided, wherein the aromatic ring of the toluene nucleus is appended to a detergent range alkyl chain in its 2-position. Since the methyl group in toluene is an ortho, para director for aromatic substitution, the detergent range olefin may attach itself in either an ortho or para position with respect to the methyl group. Subsequent sulfonation of such a mixture of ortho and para linear alkyltoluenes results in a wide range of possible isomeric products, because each of the methyl group on the ring and the detergent range alkyl group on the ring are themselves ortho, para directors. Thus, the following isomeric structures of linear alkyltoluene sulfonates are possible:



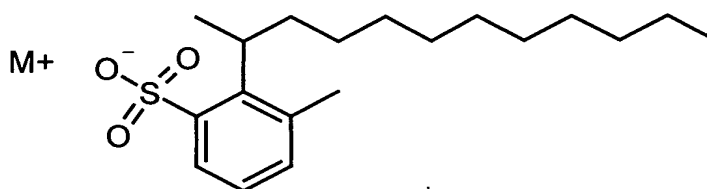
I.



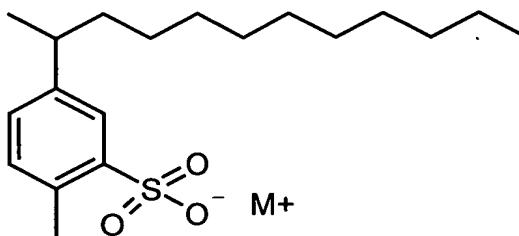
II.



III.



IV.



V.

In one aspect the present invention provides a method and catalyst for LAT (linear alkyltoluene) production having high substrate olefin conversion, high selectivity to 2-toluy l isomer LAT production, and employing a catalyst having long lifetimes and

easy handling. Through use of this aspect of the invention, 2-toluy l alkyltoluenes may be readily produced in yields in excess of 70.0 %, and indeed often in excess of 80.0 %, on the basis of catalyst selectivity.

Importantly, the present invention provides detergent compositions and cleaning formulations made with a component that comprises a mixture of sulfonated alkyltoluenes in which the hydrocarbon groups that are bonded to the toluene nucleus may comprise any number of carbon atoms in the detergent range, and in one embodiment in which at least 70.0% (weight basis) of the sulfonated alkyltoluene isomers present have the toluy l group attached to the hydrocarbon group in the 2 position of the hydrocarbon group, and in another embodiment in which at least 80.0% (weight basis) of the sulfonated alkyltoluene isomers present have the phenyl group attached to the hydrocarbon group in the 2 position of the hydrocarbon group.

The invention further provides detergent compositions and formulations which are formed from an surfactant component that comprises a mixture of the following:

- 1) a first alkyltoluene sulfonate component comprising 2-toluy l alkyltoluene sulfonates in which 2-toluy l alkyltoluene sulfonate isomers comprise any percentage between 40.0% and 80.0%, including every hundredth percentage therebetween, of all alkyltoluene sulfonate isomers present in said first alkyltoluene sulfonate component;
- and 2) a second surfactant component which may comprise: a) alkylbenzene sulfonates in which isomers having the benzene ring attached to a linear alkyl group at a position other than the alkyl group's 2 position comprise at least 60 % of all alkylbenzene sulfonate isomers present; b) alkylbenzene sulfonates in which isomers having the benzene ring attached to a linear alkyl group at a position other than the alkyl group's 2 position comprise at least 70 % of all alkylbenzene sulfonate isomers

present; or c) branched alkylbenzene sulfonates, or a combination thereof; or d) alkyltoluene sulfonates in which isomers having the toluene nucleus attached to a linear alkyl group at a position other than the alkyl group's 2 position comprise at least 60 % of all alkyltoluene sulfonate isomers present; e) alkyltoluene sulfonates in which isomers having the toluene nucleus attached to a linear alkyl group at a position other than the alkyl group's 2 position comprise at least 70 % of all alkyltoluene sulfonate isomers present; or f) branched alkyltoluene sulfonates, or a combination thereof.

Branched alkyltoluene sulfonates may be introduced into a formulated product according to the invention in one of two ways. First, a portion of the linear olefin feedstock used in the alkylation reaction of the toluene nucleus may be replaced by branched olefin(s), to provide an alkyltoluenes mixture for sulfonation in which the alkyltoluenes contain a selected amount of branched alkylate. The second method of providing branched alkyltoluene sulfonates in a finished formulation according to the invention is when branched alkyltoluenes are used as a blending component in the production of a finished product according to the invention. Thus, by either blending or providing branching in the alkylation reaction product, it is possible to provide a wide range of the amount of branched alkyltoluene sulfonates in a finished formulation according to the invention; however, it is preferable that the branched isomers comprise any amount less than 50.0 % of the total alkyltoluene sulfonate isomers present in a given formulation according to the invention. In another preferred form of the invention, branched isomers comprise any amount less than 15.00% of the total alkyltoluene sulfonate isomers present in a given formulation according to the invention. In yet another preferred form of the invention, branched

isomers comprise any amount less than 2.00% of the total alkyltoluene sulfonate isomers present in a given formulation according to the invention.

In one preferred form of the invention, lower activity isomers (isomers other than the 2-phenyl isomers) of linear alkylbenzenes or linear alkyltoluenes are present in the second surfactant component in any amount between 0.00% and 70.00%, including every hundredth percentage therebetween, by weight based upon the total weight of the second surfactant component.

In a preferred form of the invention, the second surfactant component may comprise alkyltoluene sulfonates or alkylbenzene sulfonates in which isomers having the benzene ring attached to a linear alkyl group at a position other than the alkyl group's 2 position comprise at least 50 % of all alkylbenzene sulfonate isomers present.

In another preferred form of the invention, the second surfactant component may comprise alkyltoluene sulfonates or alkylbenzene sulfonates in which isomers having the benzene ring attached to a linear alkyl group at a position other than the alkyl group's 2 position comprise at least 40 % of all alkylbenzene sulfonate isomers present.

In another preferred form of the invention, the second alkylbenzene sulfonate component may comprise alkyltoluene sulfonates or alkylbenzene sulfonates in which isomers having the benzene ring attached to a linear alkyl group at a position other than the alkyl group's 2 position comprise at least 30 % of all alkylbenzene sulfonate isomers present.

Thus, an alkylbenzene sulfonate component according to yet another embodiment of the invention may contain sulfonated 2-phenyl alkyltoluenes in an

amount of at least 30.00 % by weight based upon the total weight of the sulfonated alkyltoluene component. In another form of the invention, an alkyltoluene sulfonate component may contain sulfonated 2-phenyl alkyltoluenes in an amount of at least 40.00 % by weight based upon the total weight of the sulfonated phenyl alkyltoluene component. In yet another form of the invention, an alkyltoluene sulfonate component may contain sulfonated 2-phenyl alkyltoluenes in an amount of at least 50.00 % by weight based upon the total weight of the sulfonated alkyltoluene component. In yet another form of the invention, an alkyltoluene sulfonate component may contain sulfonated 2-phenyl alkyltoluenes in an amount of at least 60.00 % by weight based upon the total weight of the sulfonated alkyltoluene component. In yet another form of the invention, an alkyltoluene sulfonate component may contain sulfonated 2-phenyl alkyltoluenes in an amount of at least 70.00 % by weight based upon the total weight of the sulfonated phenyl alkyltoluene component. In yet another form of the invention, an alkyltoluene sulfonate component may contain sulfonated 2-phenyl alkylbenzenes in an amount of at least 80.00 % by weight based upon the total weight of the sulfonated alkyltoluene component.

By admixture with conventional mixtures of sulfonated linear alkylbenzene detergents, a mixture of sulfonated alkylbenzenes and sulfonated alkyltoluenes useful as components in detergent formulations having any desired content of the total amount of 2-phenyl alkylbenzene or 2-phenyl alkyltoluene isomers, or combination of these, in the range of between about 18.00 % and 82.00 %, including every hundredth percentage therebetween, may be produced using the materials provided according to the invention. Such mixtures of sulfonated alkylbenzenes with

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sulfonated alkyltoluenes are useful as a component in forming detergent and cleaning compositions useful in a wide variety of applications as later illustrated in the examples.

It has also been found that a catalyst according to this invention may be used in combination with an existing aluminum chloride or hydrogen fluoride alkylation facility to afford LAB or LAT having a higher 2-phenyl or 2-toluy1 isomer content than would otherwise be available from such plant using conventional catalysts. Thus, an existing facility may be retrofitted to include one or more reactors containing the fluorine-containing mordenite of this invention. In this manner, a slip stream of reactants may be sent to the mordenite with effluent therefrom being introduced back into the conventional alkylation system. This embodiment has several advantages. For example, the cost of capital is minimized since conventional equipment will already be in place. Also, the retrofitted plant can produce higher 2-phenyl isomer LAB or LAT at the discretion of its operator, depending on need. That is, the plant need not produce strictly high 2-phenyl isomer LAB or LAT and can instead produce high 2-phenyl isomer at its discretion. In one embodiment, a slip stream of reactant is drawn and sent to one or more reactors containing fluorine-containing mordenite catalyst. The effluent from the fluorine-containing mordenite reactor may then be combined with effluent from the HF or aluminum chloride reactor to provide a product having a higher level of 2-phenyl isomer LAB or LAT than would otherwise be present in product from an HF or aluminum chloride reactor.

The invention, in one broad respect, is directed at cleaning formulations designed to cleanse a wide variety of surfaces or substrates and which possess increased tolerance to water hardness, wherein the formulations comprise an alkyltoluene

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In another broad respect, this invention is a process for the production of linear alkyltoluene, comprising: a) contacting toluene and an olefin having about 8 to about 30 carbons in the presence of a fluorine-containing mordenite to form a first linear alkyltoluene stream; b) contacting toluene and an olefin having about 8 to about 30 carbons in the presence of a conventional linear alkylbenzene alkylation catalyst to form a second linear alkyltoluene stream; and c) combining the first linear alkyltoluene stream and the second linear alkyltoluene stream form a third linear alkyltoluene stream, as well as the mono-sulfonation product made from this process.

In yet another broad respect, this invention is a process for the production of linear alkyltoluene, comprising: a) dehydrogenating a paraffin to form an olefin; b) sending a primary feed stream of toluene and the olefin through a conduit to a conventional linear alkylbenzene alkylation reactor; c) contacting the primary feed

stream in the conventional linear alkylbenzene alkylation reactor with a conventional linear alkylbenzene alkylation catalyst under conditions effective to react the toluene and olefin to form a first linear alkyltoluene product; d) withdrawing a portion of the primary feed stream from the conduit and contacting the portion with a fluorine-containing mordenite under conditions effective to react the toluene and olefin to form a second linear alkyltoluene product; e) combining the first and second linear alkyltoluene products to form a crude linear alkyltoluene stream; and f) distilling the crude linear alkyltoluene stream in a first distillation column to separate toluene that did not react and to form a toluene-free linear alkyltoluene stream.

Such process may optionally include the steps of: g) distilling the toluene-free linear alkyltoluene stream in a second distillation column to separate any olefin and to form a linear alkyltoluene stream; and h) distilling the second olefin-free alkyltoluene stream in a third distillation column to provide an overhead of a purified linear alkyltoluene product and removing a bottoms stream containing any heavies.

In another broad respect, this invention is a process useful for the production of monoalkyltoluene, comprising: introducing a feed comprising olefin having about 8 to about 30 carbons and toluene into a fluorine-containing mordenite catalyst bed under conditions such that monoalkyltoluene is produced, allowing toluene, olefin, and monoalkyltoluene to descend (fall) into a reboiler from the catalyst bed, removing monoalkyltoluene from the reboiler, and heating the contents of the reboiler such that toluene refluxes to further contact the fluorine-containing mordenite.

In yet another broad aspect, this invention relates to mordenite useful for alkylating toluene with olefin having a silica to alumina molar ratio of about 10:1 to about 100:1; wherein the mordenite has been treated with an aqueous hydrogen fluoride

solution such that the mordenite contains from about 0.1 to about 4 percent fluorine by weight.

In yet another broad respect, the invention relates to a chemical mixture that contains linear alkyltoluenes produced using the process(es) and/or catalyst(s) taught herein, which chemical mixture is useful for producing a mixture of sulfonated linear alkyltoluenes which mixture contains a higher concentration of sulfonated 2-toluy l alkyltoluenes than previously available using prior art methods and catalysts.

In another broad respect, the invention comprises formulations for finished consumer and industrial strength compositions useful in or as: all-purpose cleaners, pine oil microemulsions, liquid dishwashing soaps, enzyme-based powdered and liquid laundry detergents, enzyme-free powdered laundry detergents, and the like, as it has been found that the use of sulfonated LAT mixtures having a higher content of the 2-phenyl isomer with respect to what has been heretofore available from the teachings of the prior art improves the effectiveness and cleaning action of all cleaning compositions which contain conventional sulfonated alkylbenzene detergents, be they linear or branched. This is true whether all or only a portion of the linear alkylbenzene sulfonate in the formulations of prior art are replaced by the linear alkyltoluene sulfonates of this invention having enhanced 2-phenylalkyl concentration (any percentage between 30.00% and 80.00%, including every hundredth percentage therebetween) over the materials available according to the prior art.

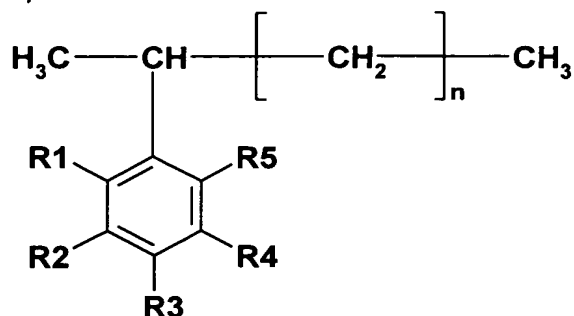
In another broad respect, the invention is a method useful for the preparation of fluorine-containing mordenite, comprising contacting a mordenite having a silica to alumina molar ratio in a range from about 10:1 to about 100:1 with an aqueous hydrogen fluoride solution having a concentration of hydrogen fluoride in the range of

from about 0.1 to about 10 percent by weight such that the mordenite containing fluorine is produced, collecting the fluorine-containing mordenite by filtration, and drying.

The fluorine treated mordenite catalyst advantageously produces high selectivities to the 2-phenyl isomer in the preparation of LAB and LAT, generally producing selectivities of about 70 percent or more. Also, the fluorine treated mordenite enjoys a long lifetime, preferably experiencing only a 25 percent or less decrease in activity after 400 hours on stream. A process operated in accordance with the apparatus depicted in FIGS. 1 and 2 has the advantage that rising toluene from the reboiler continuously cleans the catalyst to thereby increase lifetime of the catalyst. In addition, this invention advantageously produces only low amounts of dialkyltoluene, which is not particularly as useful for detergent manufacture, as well as only low amounts of tetralin derivatives.

In another aspect the invention provides solid salts of alkyltoluene sulfonates, which solid salts may contain various cations necessary for charge balance.

In another aspect the invention comprises finished detergent compositions useful for cleaning fabrics, dishes, hard surfaces, and other substrates that is formed from components comprising: a) an alkyltoluene sulfonate surfactant component present in any amount between 0.25 % and 99.50 % by weight based upon the total weight of the finished detergent composition, said component characterized as comprising any amount between 26.00 % and 82.00 % by weight based upon the total weight of the component, and including every hundredth percentage therebetween, of water-soluble sulfonates of the 2-phenyl isomers of alkyltoluenes described by the general formula:



wherein n is equal to any integer between 4 and 16, wherein one and only one of R₁, R₂, R₃, R₄ and R₅ is a sulfonate group, and wherein one and only one of R₁, R₂, R₃, R₄ and R₅ is a substituent group selected from the group consisting of methyl and ethyl; and b) any amount between 0.50 % and 99.75 % of other components known to be useful in formulating soaps, detergents, and the like, wherein at least one of said other components is selected from the group consisting of: fatty acids, alkyl sulfates, an ethanolamine, an amine oxide, alkali carbonates, water, ethanol, isopropanol, pine oil, sodium chloride, sodium silicate, polymers, alcohol alkoxylates, zeolites, perborate salts, alkali sulfates, enzymes, hydrotropes, dyes, fragrances, preservatives, brighteners, builders, polyacrylates, essential oils, alkali hydroxides, ether sulfates, alkylphenol ethoxylates, fatty acid amides, alpha olefin sulfonates, paraffin sulfonates, betaines, chelating agents, tallowamine ethoxylates, polyetheramine ethoxylates, ethylene oxide/propylene oxide block copolymers, alcohol ethylene oxide/propylene oxide low foam surfactants, methyl ester sulfonates, alkyl polysaccharides, N-methyl glucamides, alkylated sulfonated diphenyl oxide, and water soluble alkylbenzene sulfonates or alkyltoluene sulfonates having a 2-phenyl isomer content of less than 26.00 %.

The mordenite catalyst of the present invention is useful as a catalyst in the production of LAT's in accordance with the process of manufacturing LAT's of this invention. LAT is useful as starting material to produce sulfonated LAT, which itself is useful as a surfactant.

Certain terms and phrases have the following meanings as used herein:

"Meq/g" means milliequivalents of titratable acid per gram of catalyst, which is a unit used to describe acidity of the catalysts. Acidity is generally determined by titration with a base, as by adding excessive base, such as sodium hydroxide, to the catalyst and then back titrating the catalyst.

"Conv." and "Conversion" mean the mole percentage of a given reactant converted to product. Generally, olefin conversion is about 95 percent or more in the practice of this invention.

"Sel." and "Selectivity" mean the mole percentage of a particular component in the product. Generally, selectivity to the 2-phenyl isomer is about 70 % or more in the practice of this invention.

"Detergent range" means a molecular species which contains an alkyl group that comprises any number of carbon atoms: 8, 9, 10, 11, 12, 13, 14 or 15 per alkyl group, and includes LAB, LAB sulfonates, LAT, LAT sulfonates, and mono-olefins.

"Substantially linear" when referring to a hydrocarbon or alkyl chain that is part of an alkylbenzene or alkyltoluene, whether the alkylbenzene or alkyltoluene is sulfonated or not, means a hydrocarbon comprising between 7 and 16 carbon atoms linked to one another to form a straight chain, wherein the carbon atoms of said straight chain may have only hydrogen atoms or a methyl group bonded to them as appendages.

"Branched alkyl" when referring to a hydrocarbon or alkyl chain that is part of an alkylbenzene or alkyltoluene, whether the alkylbenzene or alkyltoluene is sulfonated or not, means a hydrocarbon comprising between 4 and 16 carbon atoms linked to one another to form a straight chain, wherein one or more of the carbon atoms of said straight chain may have a hydrogen atom and any alkyl group other than a methyl group (including without limitation ethyl, propyl and butyl groups), bonded to them as appendages.

"Branched alkylbenzene" means a molecular species which comprises a branched alkyl chain appended to a benzene ring.

"Branched alkyltoluene" means a molecular species which comprises a branched alkyl chain appended to a the ring portion of a toluene molecule, regardless of the respective positions of the methyl group of the toluene and the branched alkyl chain.

"Branched alkylbenzene sulfonate" means a water-soluble salt of a branched alkylbenzene that has been sulfonated.

"Branched alkyltoluene sulfonate" means a water-soluble salt of a branched alkyltoluene that has been sulfonated, regardless of the isomeric position of the sulfonate group and the alkyl group with respect to the methyl group.

"2-phenyl alkylbenzenes" means a benzene ring having at least one alkyl group attached to it, wherein the alkyl group comprises any number of carbon atoms between 7 and 16 (including every integral number therebetween) linked to one another so as to form a substantially linear chain and wherein the benzene ring is attached the alkyl group at a carbon atom that is adjacent to the terminal carbon of the substantially linear chain. Thus, the carbon atom that is attached to the benzene ring has a methyl group and another alkyl group attached to it in a 2-phenyl alkylbenzene.

"2-phenyl alkyltoluenes" means a toluene molecule having, in addition to its methyl group, at least one other alkyl group attached to it, wherein the other alkyl group comprises any number of carbon atoms between 7 and 16 (including every integral number therebetween) linked to one another so as to form a substantially linear chain and wherein the ring portion of the toluene molecule is attached the alkyl group at a carbon atom that is adjacent to the terminal carbon of the substantially linear alkyl chain. Thus, the carbon atom that is attached to the ring of the toluene has a methyl group and another alkyl group attached to it in a 2-phenyl alkyltoluene. 2-phenyl alkyltoluene is synonymous with 2-tolyl alkylbenzene.

"2-tolyl alkylbenzene" means a toluene molecule having, in addition to its methyl group, at least one other alkyl group attached to it, wherein the other alkyl group comprises any number of carbon atoms between 7 and 16 (including every integral number therebetween) linked to one another so as to form a substantially linear chain and wherein the ring portion of the toluene molecule is attached the alkyl group at a carbon atom that is adjacent to the terminal carbon of the substantially linear alkyl chain. Thus, the carbon atom that is attached to the ring of the toluene has a methyl group and another alkyl group attached to it in a 2-phenyl alkyltoluene.

"Sulfonated 2-phenyl alkylbenzenes" means 2-phenyl alkylbenzenes as defined above which further comprise a sulfonate group attached to the benzene ring of a 2-phenyl alkylbenzene as described above, regardless of the position of the sulfonate group on the ring with respect to the location of the alkyl group; however, it is most common and preferred that the sulfonate group is attached to the benzene ring in the para-position with respect to the alkyl group.

"Sulfonated 2-phenyl alkyltoluenes" means 2-phenyl alkyltoluenes as defined above which further comprise a sulfonate group attached to the aromatic ring of a 2-phenyl alkyltoluene as described above, regardless of the positions of the sulfonate group, the methyl group, and the alkyl group with respect to one another; however, it is most preferred that the sulfonate group is attached to the benzene ring in the para-position with respect to the alkyl group.

"LAB" means a mixture linear alkylbenzenes which comprises a benzene ring appended to any carbon atom of a substantially linear alkyl chain in the detergent range.

"LAT" means a mixture linear alkyltoluenes which comprises a toluene molecule having its aromatic ring appended to any carbon atom of a substantially linear alkyl chain in the detergent range.

"LAB sulfonates" means LAB which has been sulfonated to include an acidic sulfonate group appended to the benzene rings (thus forming a parent acid), and subsequently rendered to a form more soluble to aqueous solution than the parent acid by neutralization using any of alkali metal hydroxides, alkaline earth hydroxides, ammonium hydroxides, alkylammonium hydroxides, or any chemical agent known by those skilled in the art to react with linear alkylbenzene sulfonic acids to form water-soluble linear alkylbenzene sulfonates.

"LAT sulfonates" means LAT which has been sulfonated to include an acidic sulfonate group appended to the aromatic ring of the LAT (thus forming a parent acid), and subsequently rendered to a form more soluble to aqueous solution than the parent acid by neutralization using any of alkali metal hydroxides, alkaline earth hydroxides, ammonium hydroxides, alkylammonium hydroxides, or any chemical agent known by

those skilled in the art to react with linear alkylbenzene sulfonic acids to form water-soluble linear alkylbenzene sulfonates.

"2-phenyl isomer" means LAB or LAT sulfonates of 2-phenyl alkylbenzenes, as warranted by the context.

"sulfonated aromatic alkylate" means a chemical compound which comprises a benzene ring having a sulfonate group attached to a carbon atom of the ring structure and at least one alkyl group in the detergent range attached to a carbon atom of the ring structure; hence LAT and LAB materials fall within this classification.

All percentages set forth in this specification and its appended claims are expressed in terms of weight percent, unless specified otherwise.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a representation of a first continuous reactive distillation column employed in the practice of this invention;

FIG. 2 shows a representation of a second continuous reactive distillation column employed in the practice of this invention;

FIG. 3 shows a representative process scheme for one embodiment of this invention where a conventional LAB alkylation reactor (that is also useful in producing LAT) is shown in combination with a fluorine-containing mordenite reactor of this invention wherein a slip stream of reactant to the conventional reactor is sent to the mordenite reactor and wherein the flow of high 2-phenyl isomer LAB or LAT, as the case may be, from the mordenite reactor may be adjusted to vary the 2-phenyl isomer LAB or LAT content of the effluent from the conventional LAB alkylation reactor.

FIG. 4 shows another representative process scheme for one embodiment of this invention where a first conventional LAB alkylation reactor (also useful in LAT production) is shown in combination with a fluorine-containing mordenite reactors of this invention wherein a slip stream of reactant to the conventional reactor is sent to one or both of a pair of mordenite reactor and wherein the LAT or LAB effluent from the first LAB alkylation reactor and the effluent from the one or both mordenite reactors are combined and flowed into a second conventional LAB alkylation reactor.

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FIG. 5 shows graphic data of a total detergency study conducted on cloth swatches using detergents having alkylbenzenes of differing 2-phenyl isomer content.

FIG. 6 shows the turbidity of solutions containing conventional alkylbenzene surfactant in aqueous solutions of differing hardness;

FIG. 7 shows the turbidity of solutions containing alkylbenzene surfactant having a 2-phenyl isomer content of about 80% in aqueous solutions of differing hardness;

FIG. 8 shows the turbidity of aqueous solutions having a constant water hardness in the presence of different mixtures which each contain different amounts of linear alkylbenzene sulfonates and linear alkyltoluene sulfonates in which the 2-phenyl isomer content of the alkylbenzene sulfonates and the alkyltoluene sulfonates is greater than 80% by weight based upon the total weight of all sulfonates present.

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DETAILED DESCRIPTION OF THE INVENTION

The catalysts used to prepare the linear alkyltoluenes of this invention is a fluorine-containing mordenite. Mordenite is a type of zeolite. The catalyst of this invention is prepared from hydrogen mordenite (typically having 0.1 percent or less of sodium) having a silica-alumina molar ratio of from about 10:1 to about 100:1. More typically, the starting mordenite has a silica/alumina molar ratio of from about 10:1 to about 50:1. The starting hydrogen mordenite, which is commonly available commercially, is treated with an aqueous solution of hydrogen fluoride ("HF") to produce the active, long-life and highly selective catalyst of the invention. In the course of such HF treatment, as well as during subsequent calcination of said HF-treated mordenite, the silica/alumina molar ratio typically increases. The finished catalysts of this invention show a fluorine content of from about 0.1 to about 4 percent by weight, more typically about 1 percent.

The aqueous solution used to treat the mordenite may contain a range of HF concentrations. Generally, the HF concentration is a minimum of about 0.1 percent by weight. Below such minimum concentration, the effect of the fluorine treatment significantly decreases, resulting in the undesirable need for repeated treatments. Generally, the HF concentration on the upper end is about 10 percent by weight or less. Above a concentration of about 10 percent by weight, the HF is so concentrated that it is difficult to prevent HF from destroying the crystallinity of the mordenite, thereby detrimentally affecting its efficacy as a catalyst for LAB and LAT production.

The aqueous HF solution may be prepared by diluting commercially available 48% HF solutions to the desired concentration. Alternatively, HF can be sparged into water to provide an aqueous HF solution.

Typically, the treatment is carried out by adding mordenite powder or pellets to a stirred aqueous HF solution at a temperature of from about 0°C to about 50°C. The stirring and contacting is continued for a time sufficient to achieve the desired level of fluorine in the mordenite. This time may vary depending on factors such as HF concentration, amount of HF solution relative to the amount of mordenite being treated, speed of agitation is employed, and temperature. After treatment, the mordenite can be recovered by filtration, and then dried. It is also possible to impregnate the mordenite to incipient wetness with a given HF solution, as well as to treat the mordenite with gaseous hydrogen fluoride. Preferably said fluoride-treated mordenite would be calcined in air prior to use in alkylation service. The preferred calcination temperature would be in the range from about 400°C to about 600°C. Alternative mordenite fluorinating agents to hydrofluoric acid and hydrogen fluoride include ammonium fluoride, fluorided silicon compounds and fluorided hydrocarbons.

The HF-treated mordenite of this invention generally has about 0.1 percent by weight or more of fluorine based on the total weight of the mordenite. Typically, the fluorine-containing mordenite contains about 4 percent by weight or less fluorine. The fluorine-containing mordenite most typically contains about 1 percent by weight of fluorine.

The mordenite can be used in the practice of this invention as a powder, in pellet form, as granules, or as extrudates. The mordenite can be formed into pellets or

extrudates using binders well known to those of skill in the art, such as alumina, silica or mixtures thereof.

Reactants for LAT Production

In the practice of this invention, toluene is alkylated with olefin to form LAT. These reactants can be handled and purified as is generally performed by those of ordinary skill in the art. In this regard, it is preferred that the reactants are water and alcohol free. The olefins employed in the practice of this invention have from about 8 to about 30 carbons, preferably from about 10 to about 14 carbons, such as is available commercially or produced as dehydrogenated paraffin feed stocks. It is preferred that the olefin be monounsaturated. It is most preferred that the olefin be an alpha-olefin containing a terminal ethylenic unit.

Olefins in the 10 to 14 carbon number range are typically available from the dehydrogenation of a C₁₀ to C₁₄ paraffin mixture using methods known to those skilled in the art. Dehydrogenation of such paraffins provides a mixture of mono-olefins having a double bond at the terminal carbon in the chain and its neighboring carbon atom, and leaves some of the paraffins unconverted. Thus, the effluent of a dehydrogenation reactor into which was fed a C₁₀ to C₁₄ mixture typically comprises a mixture which is predominantly paraffins and has an olefin content of about 5 to 20%, and is readily available. Often, the olefin content of said olefin-paraffin mixture may be 8 to 10 weight %.

The process of this invention for producing the 2-phenyl isomer of the LAT having the formula previously set forth above can be carried out using the continuous reactive distillation column depicted in **FIG. 1**. In **FIG. 1**, a feed mixture of toluene and olefin, generally at a toluene-to-olefin molar ratio range of about 1:1 to 100:1 flows

from feed pump **10** to feed inlet **14** via line **12**. The feed mixture falls to packed mordenite catalyst bed **32** where alkylation in the presence of the fluorine-containing mordenite occurs. Alternatively, while not depicted in **FIG. 1**, the toluene and olefin can be introduced separately into the bed with mixing occurring in the bed, or the reactants can be mixed via an in-line mixer prior to introducing the reactants into the catalyst bed, or the reactants can be injected separately above the bed with mixing affected by use of standard packing above the bed, or the reactants can be sparged into the chamber above the bed. The catalyst bed **32** depicted in **FIG. 1** for laboratory scale may be made of two lengths of 1.1 inch internal diameter tubing, the lengths being 9.5 inches and 22 inches. In the catalyst bed **32**, the falling feed mixture also contacts rising vapors of unreacted toluene which has been heated to reflux in reboiler **42** by heater **40**. Such rising vapors pass over thermocouple **38** which monitors temperature to provide feedback to heater **40**. The rising vapors of toluene and/or olefin also pass through standard packing **36** (e.g., 7.5 inches of goodloe packing). The rising vapors heat thermocouple **30** which connects to bottoms temperature controller **28** which activates heater **40** when temperature drops below a set level.

Prior to startup, the system may be flushed with nitrogen which enters via line **54** and which flows through line **58**. After startup, a nitrogen blanket is maintained over the system. Also prior to startup and during nitrogen flush, it may be desirable to heat catalyst bed **32** so as to drive off water from the fluorine-containing mordenite.

Residual water from the feed mixture or which otherwise enters the system is collected in water trap **24** upon being liquefied at condenser **21** (along with benzene vapor). If the feed is very dry (free of water) the water trap **24** may not be needed. Removing water leads to longer catalyst lifetime. Hence, the water trap **24** is optional.

The same applies to **FIG. 2**. Condenser **21** is cooled via coolant such as water entering condenser **21** via port **22** and exiting via port **20**. As needed, water in water trap **24** may be drained by opening drain valve **26**.

As needed, when LAT content in reboiler **42** rises to a desired level, the bottoms LAT product may be removed from the system via line **47**, using either gravity or bottoms pump **48** to withdraw the product. When product is so withdrawn, valve **44** is opened.

In **FIG. 1**, dip tube **46**, which is optional, is employed to slightly increase the pressure in reboiler **42** to thereby raise the boiling point of benzene a degree or two. Likewise, a pressure generator **56** may be optionally employed to raise the pressure of the system. Other standard pressure increasing devices can be employed. Pressure can thus be increased in the system such that the boiling point of toluene increases up to about 200°C.

In **FIG. 1**, control mechanisms for heat shutoff **50** and pump shutoff **52** are depicted which serve to shut off heat and pump if the liquids level in the system rises to such levels. These control mechanisms are optional and may be included so that the catalyst bed does not come into contact with the bottoms of the reboiler. Line **60** connects pump shutoff **52** to the system above condenser **21**.

In the practice of this invention in the alkylation of toluene, a wide variety of process conditions can be employed. In this regard, the temperature in the catalyst bed may vary depending on reactants, rate of introduction into the catalyst bed, size of the bed, and so forth. Generally, the bed is maintained at the reflux temperature of toluene depending on pressure. Typically, the temperature of the catalyst bed is above about 100°C, and most likely about 110° to 130°C or more in order to have reasonable

reaction rates, and about 250°C or less to avoid degradation of reactants and products and to avoid deactivation of the catalyst by coke build-up. Preferably, the temperature is in the range from about 120°C to about 200°C. The process may be operated at a variety of pressures during the contacting step, with pressures of about atmospheric most typically being employed. When the process is operated using a system as depicted in FIGS. 1 and 2, the reboiler temperature is maintained such that toluene and olefin vaporize, the temperature varying depending on olefin, and generally being from about 110°C to about 300°C for olefins having 10 to 14 carbons. The composition of the reboiler will vary over time, but is generally set initially to have a toluene-to-olefin ratio of about 5:1, with this ratio being maintained during the practice of this invention. The rate of introduction of feed into the catalyst bed may vary, and is generally at a liquid hourly space velocity ("LHSV") of about 0.05 hr⁻¹ to about 10 hr⁻¹, more typically from about 0.05 hr⁻¹ to about 1 hr⁻¹. The mole ratio of toluene to olefin introduced into the catalyst bed is generally from about 1:1 to about 100:1. In commercial toluene alkylation operations, it is common to run at mole ratios of from about 2:1 to about 20:1, which can suitably be employed in the practice of this invention, and to charge said olefins as an olefin-paraffin mixture comprising 5% to 20% olefin content. Said olefin-paraffin mixtures are normally generated commercially through dehydrogenation of the corresponding paraffin starting material over a noble metal catalyst.

Another continuous reactive distillation apparatus is depicted in **FIG. 2**. In **FIG. 2**, the feed mixture enters the reactor via feed inlet **114**. The feed mixture falls through the column into catalyst bed **132**, wherein alkylation to form LAT occurs. A thermowell **133** monitors the temperature of said catalyst bed **132**. The catalyst bed **132** may be optionally heated externally and is contained within 1-1/4 inch stainless steel

tubing. Goodloe packing is positioned at packing **136** and **137**. LAT product, as well as unreacted toluene and olefin, fall through packing **136** into reboiler **142**. In reboiler **142**, electric heater **140** heats the contents of reboiler **142** such that heated vapors of toluene and olefin rise from the reboiler **142** to at least reach catalyst bed **132**. As needed, the bottoms LAB product may be removed from reboiler **142** by opening bottoms valve **144** after passing through line **147** and filter **145**. Residual water from the feed mixture, or which otherwise enters the system, may be condensed at condenser **121** which is cooled with coolant via outlet line **122** and inlet line **120**. The condensed water falls to water trap **124**, which can be drained as needed by opening drain valve **126**. Temperature in the system is monitored via thermocouples **138**, **130**, and **165**. The system includes pressure release valve **166**. A nitrogen blanket over the system is maintained by introduction of nitrogen gas via inlet line **154**. Level control activator **150** activates bottoms level control valve **151** to open when the liquids level in the reboiler rises to the level control activator **150**. Line **160** connects level control activator **150** to the system above condenser **121**.

While the systems depicted in **FIG. 1** and **FIG. 2** show single catalyst bed systems, it may be appreciated that multi-catalyst bed reactors are within the scope of this invention, as well as multiple ports for inlet feeds, water traps, product removal lines, and so forth. Moreover, the process may be run in batch mode, or in other continuous processes using plugflow designs, trickle bed designs, and fluidized bed designs.

It is believed that as average molecular weight of olefins increases, particularly when the average number of carbons exceed **14**, the selectivity and conversion to LAT, especially LAT with the 2-isomer, may incrementally decrease. If desired, the product

of the alkylation using HF-treated mordenite may be sent to a second, finishing catalyst bed to improve yield. This procedure is optional and is believed to be dependent on the needs and desires of the end user. An example of such a second catalyst is HF-treated clay such as montmorillonite clay having about 0.5% fluoride. Such a catalyst may also serve to lower the bromine number of the alkylate product below about 0.1, depending on conditions.

Variable 2-phenyl Isomer Content of Product Using the Mordenite of the Invention In Combination with Conventional LAT Alkylation

The fluorine-containing mordenite of this invention generally produces LAT having high 2-phenyl isomer content, such as higher than about 70%. Currently, LAT purchasers who make detergents would prefer to use LAT having a 2-phenyl isomer content in the range from about 30 to about 40 percent, but this level is not available in the marketplace. Conventional LAT alkylation technology do not achieve these higher 2-phenyl isomer levels. HF, which is currently the most widely used catalyst for production of LAT on a commercial scale, produces about 16-18 percent of the 2-phenyl isomer in the product stream from the reactor. Aluminum chloride, in contrast, produces about 26-28 percent of the 2-phenyl isomer. The present inventors recognized that a need exists for a process which produces a 2-phenyl isomer product in the desired range.

It has now been found that the mordenite of this invention can be used in combination with conventional LAB alkylation catalysts, such as HF and aluminum chloride alkylation catalysts. This may be affected by withdrawing a slip stream of reactant that is being sent to the conventional LAB reactor, and directing the slip stream to the mordenite reactor. Since conventional LAB catalysts produce product having a 2-phenyl isomer content much less than that from mordenite of this invention, combining

the LAT products from each catalyst results in a product having a higher 2-phenyl isomer content than that from the conventional LAB alkylation catalyst. For example, while the catalyst of this invention typically produces a 2-phenyl isomer content of 70% or more, a typical HF process produces about 16-18% of the 2-phenyl isomer. By combining effluent from each catalyst at given proportions, the resulting mixture will have any desired 2-phenyl isomer content in the range between the 2-phenyl isomer contents of the HF catalyst product and the mordenite catalyst product. Thus, the levels of 2-phenyl isomer may be adjusted by the amount of reactants sent to the mordenite catalyst and/or by storing 2-phenyl isomer product from the mordenite catalyst for later mixing with the product of from the conventional LAB alkylation catalyst to thereby achieve any desired level of 2-phenyl isomer content in the final product. An advantage of this invention pertains to the ability to retrofit an existing, conventional LAB system with a reactor containing fluorine-treated mordenite of this invention. This enables existing users of the conventional LAB technology to augment their existing facilities without interrupting their production. This provides a considerable cost advantage to the producer.

The conventional LAB catalysts used most frequently are HF alkylation reactors and aluminum chloride alkylation catalysts. Other alkylation catalysts include various zeolites, alumina-silica, various clays, as well as other catalysts.

FIG. 3 depicts a representative, non-limiting scheme for practice of this invention wherein the fluorine-treated mordenite is used in combination with a HF alkylation reactor to afford LAT having high 2-phenyl isomer contents relative to that produced from the HF reactor alone. The scheme of **FIG. 3** is shown in the context of LAT alkylation based on a feed from a paraffin dehydrogenation facility. Prior to this

invention, the plant depicted in **FIG. 3** would be operated conventionally without use of mordenite reactor **220**.

Thus, in conventional operation, fresh paraffin is fed to conventional dehydrogenation apparatus **210** via line **211**, with recycled paraffin being introduced from the paraffin column **250** via line **252**. Dehydrogenated paraffin from the dehydrogenation apparatus **210** is then pumped into a conventional alkylation reactor **230** containing conventional LAB catalyst, such as HF, via conduit **214**. The dehydrogenated paraffin feed may of course be supplied from any provider. The source of dehydrogenated paraffin (olefin) is not critical to the practice of this invention. LAT product from alkylation unit **230** may thereafter be purified by a series of distillation towers.

In this regard, alkylation effluent is delivered to a toluene column **240** by way of line **231**. It should be appreciated that the alkylation product may be sent offsite for purification. Further, the particular purification scheme used is not critical to the practice of this invention, but is depicted in **FIG. 3** as representative of a typical commercial operation. In **FIG. 3**, unreacted toluene is distilled off from the crude LAT product. Toluene is then recycled to the alkylation reactor **230**. The toluene-free LAT crude product from the toluene column **240** is pumped through line **241** to paraffin column **250** where any paraffin present is distilled off, with the distilled paraffin being recycled to paraffin dehydrogenation unit **210** via line **252**. Paraffin-free crude LAT alkylate from the paraffin column **250** is transported to a refining column **260** where purified LAT is distilled and removed via line **262**. Heavies (e.g., dialkylates and olefin derivatives) are withdrawn from refining column **260** via conduit **261**.

In the practice of this invention, a fluorine-treated mordenite containing reactor **220** is used in conjunction with the conventional alkylation reactor **230**. In the embodiment of this invention depicted in **FIG. 3**, a slip stream of toluene/dehydrogenated paraffin feed is taken from line **214** and pumped through mordenite reactor **220** where high 2-phenyl isomer production is achieved. LAT product from reactor **220**, high in 2-phenyl isomer, is then introduced back into line **214** via line **222**. Alternatively mordenite reactor **220** may be fed toluene and dehydrogenated paraffin (olefin) directly, rather than by way of a slip stream from line **221**. In addition, effluent from reactor **220** may, in the alternative if no unreacted olefin is present, be sent directly to toluene column **240**, for later combination with conventional alkylation reactor **230** product or transported and tied into conduit **231**, which feeds toluene column **240**. It should be appreciated that columns **240**, **250**, and **260** may be maintained at conditions (e.g., pressure and temperature) well known to those of skill in the art and may be packed with conventional materials if desired.

FIG. 4 depicts an alternative configuration to that shown in **FIG. 3**. In **FIG. 4**, dual mordenite beds **320**, **321** are used in conjunction with conventional alkylation reactors **330**, **340**. Conveniently, one of the mordenite reactors may be in operation while the other reactor is down for catalyst regeneration. For example, during operation, olefin feed (dehydrogenated paraffin) is supplied via line **301**, with toluene or other aromatic feed stock being provided via line **302**. The admixed reactants may flow to standard alkylation reactor **330** via line **304b** after passing through heat exchanger **303**. A portion of the mixed stream may be withdrawn via line **304a** for supply to the mordenite reactor. The extent of the mixed feed stream being withdrawn may be varied depending on the desired level of 2-phenyl isomer in the

final product. In another embodiment, the product from the reactor containing mordenite **320**, **321** may be fed to the first alkylation reactor **330**, particularly if the second alkylation reactor **34** is not employed in the process.

The slip stream reactants may optionally be sent to dewatering unit **317** by application of pump **306** after passing through heat exchanger **305**. In the dewatering unit **317**, water is distilled from the reactants in dewatering tower **310**. Rising vapor exits via line **311a** and passes through heat exchanger **312** wherein condensation occurs. Effluent from heat exchanger **312** is advanced to water trap **318** via line **311b**. Water is removed from water trap **318** via line **313**, with the bottom organic layer being returned to the dewatering tower **310**. Dewatered reactants may be removed via line **316** and conveyed to either line **316a** or line **316b**. Some of the dewatered reactant may be withdrawn by conduit **314b**, sent through heat exchanger **315** and returned to the tower **310** via line **314a**. In this regard, heat exchanger **315** may serve as a reboiler.

After reaction in either reactor **320** or **321**, LAT product is sent to lines **322** and **331** from either line **322a** or **322b** after passing through heat exchanger **323**. When desired, one of the catalyst beds may be regenerated, as by calcination for example, through use of regeneration heater **350**, which may be connected to the reactor of choice by dotted line **351** through valving and hardware that are not shown. The reactors **320** and **321** may optionally be run simultaneously. The reactors **320** and **321** may be loaded with mordenite catalyst in any fashion, as would be apparent to one of skill in the art. Typically, a plugged flow arrangement is used. The amount of catalyst employed may vary depending on a variety of considerations such as type and flow rate of reactants, temperature and other variables. The combined effluents

from conventional reactor 330 and mordenite reactors 320 or 321 may be fed to a second conventional reactor 340, or optionally may be sent to a purification section directly if no unreacted olefin is present (the conventional reactor serves to complete reaction of any olefin that is not converted in the mordenite reactors 320, 321). In FIG. 4, effluent from the second conventional alkylation reactor is advanced to a purification section. The second alkylation reactor may be used to react unreacted feed stock from reactors 330, 320 and 321 to thereby reduce recycle loads.

It should be appreciated that a wide variety of configurations are contemplated, and the figures should not be construed as limiting this invention or claims hereto. Additional reactors and other equipment may, for example, be used.

The following examples are illustrative of the present invention and are not intended to be construed as limiting the scope of the invention or the claims. Unless otherwise indicated, all percentages are by weight. In the examples, all reactants were commercial grades and used as received. The apparatus depicted in FIG. 1 was employed for examples 2-4. The apparatus depicted in FIG. 1 was used for example 5.

While the examples herein relate to the alkylation of benzene according to the invention to provide LAB having enhanced 2-phenyl isomer content, the same catalysts and equipment may be used to provide LAT using toluene as a starting material in the stead of benzene, using the temperatures mentioned above for LAT production.

It may be noted that example 2 illustrates LAB production from paraffin dehydrogenate using the fluoride-treated mordenite catalyst of example B, where good catalyst life (250+ hrs) is achieved without catalyst regeneration, while maintaining a 2-phenyl isomer selectivity of >70% and high LAB productivity without significant loss of fluoride. Comparative example 1, on the other hand, using untreated mordenite, with

no fluoride added, shows a rapid decline in LAB production. In addition, examples 3 and 4 illustrate LAB production using a 5:1 molar benzene/C₁₀-C₁₄ olefin feed mix and the fluoride-treated mordenite catalysts of Example B when operating at different LHSV's in the range of 0.2-0.4 hr⁻¹. Catalyst life may exceed 500 hours. Example 5 illustrates LAB production with the fluoride-treated mordenite catalyst where the alkylation is conducted at higher temperatures and under pressure. Examples 6-8 illustrate the performance of three HF-treated mordenite catalysts with different fluoride loadings. Example 9 shows how virtually no alkylation activity is observed with a highly-fluorinated mordenite.

EXAMPLE A

This example illustrates the preparation of a hydrogen fluoride-modified mordenite.

To 30 g of acidified mordenite (LZM-8, SiO₂/Al₂O₃ ratio 17; Na₂O wt% 0.02, surface area 517 m²/g, powder, from Union Carbide Corp.) was added 600 ml of 0.4% hydrofluoric acid solution, at room temperature. After 5 hours the solid zeolite was removed by filtration, washed with distilled water, dried at 120°C overnight, and calcined at 538°C.

EXAMPLE B

The example illustrates the preparation of a hydrogen fluoride-modified mordenite.

To 500 g of acidified, dealuminized, mordenite (CBV-20A from PQ Corp.; SiO₂/Al₂O₃ molar ratio 20; Na₂O, 0.02 wt%; surface area 550 m²/g, 1/16" diameter extrudates, that had been calcined at 538°C, overnight) was added a solution of 33 ml of 48% HF solution in 1633 ml of distilled water, the mix was cooled in ice, stirred on a

rotary evaporator overnight, then filtered to recover the extruded solids. The extrudates were further washed with distilled water, dried in vacuo at 100°C, and then calcined at 538°C, overnight.

Analyses of the treated mordenite showed:

F: 1.2%;

Acidity: 0.49 meq/g

EXAMPLE 1

This example illustrates the preparation of linear alkylbenzenes using a hydrogen fluoride-modified mordenite catalyst.

To a 500 ml flask, fitted with condenser and Dean Stark Trap was added 100 ml of benzene (reagent grade) plus 10 g of hydrogen fluoride-modified mordenite zeolite, prepared by the method of Example A. The mix was refluxed for 15-20 minutes to remove small amounts of moisture, then a combination of benzene (50 ml) plus 1-dodecene (10 g) was injected into the flask and the solution allowed to reflux for 3 hours.

Upon cooling, the modified mordenite catalyst was removed by filtration, the filtrate liquid flashed to remove unreacted benzene, and the bottoms liquid analyzed by gas chromatography.

Typical analytical data are summarized in Table 1.

DODECENE CONV. (%)	LAB ISOMER DISTRIBUTION (%)					HEAVIES (%)	LINEAR LAB (LLAB) (%)
	2-Ph	3-Ph	4-Ph	5-Ph	6-Ph		
99.7	79.9	16.6	0.8	1.3	1.3	0.2	95.9

Table 1

EXAMPLE 2

This example illustrates the preparation of linear alkylbenzenes from paraffin dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

In example 2, benzene was alkylated with a sample of C₁₀-C₁₄ paraffin dehydrogenate containing about 8.5% C₁₀-C₁₄ olefins. Alkylation was conducted in a process unit as shown in FIG. 1.

Alkylation was conducted by first charging 500 ml of a benzene/paraffin dehydrogenate mix (10:1 molar ratio, benzene/C₁₀-C₁₄ olefin) to the reboiler and 250 cc of the HF-treated mordenite of example B to the 1.1" i.d. reaction zone. The mordenite was held in place using Goodloe packing. The reboiler liquid was then heated to reflux and a benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix (10:1 molar ratio, benzene/C₁₀-C₁₄ olefin) continuously introduced into the unit above the catalyst column at the rate of 100 cc/hr. (LHSV=0.4 hr⁻¹).

Under steady state, reflux, conditions liquid product was continuously withdrawn from the reboiler and water continuously taken off from the water trap. The crude liquid product was periodically analyzed by gas chromatography. The reboiler temperature was typically in the controlled range of 97-122°C. The column head temperature variability was 78-83°C. A summary of the analytical results may be found in Table 2.

After 253 hours on stream, the recovered HF-treated mordenite catalyst showed by analysis: F: 1.1%; Acidity: 0.29 meq/g; H₂O: 0.3%

Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel.(%)	C ₆ H ₆ Conc. (%)
0	0	1.4		32.3
2	1	3.4		19.7
4	2	5.8	74.9	16.6
6	3	6.6	75.8	25.2
32	4	7.9	80.7	27.0
56	5	7.8	82.7	27.0
69	6	7.3	81.4	27.4
94	7	6.5	82.0	27.8
118	8	6.0	78.4	27.7
142	9	5.9	81.3	26.9
166	10	5.4	81.5	27.3
207	11	5.3	81.3	26.1
229	12	5.1	81.1	27.4
253	13	4.9	81.4	28.1

Table 2

Comparative Example 1

This example illustrates the preparation of linear alkylbenzene from paraffin dehydrogenate using an untreated mordenite catalyst. Following the procedures of Example 9, the alkylation unit was charged with 250 cc of untreated, calcined, mordenite, (the starting mordenite of Example B), and the liquid feed comprised benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 10:1 molar ratio of benzene/C₁₀-C₁₄ olefin.

Typical results are summarized in Table 3.

The recovered mordenite showed by analysis: Acidity: 0.29 meq/g; H₂O: 2.1%

Time on Stream (Hrs)	Sample	Alkylate Conc.(%)	2-Phenyl sel.(%)	C ₆ H ₆ Conc. (%)
0	0			11.2
2	1	6.50		9.9
4	2	7.16	73.2	17.1
6	3	7.09	73.1	26.4
22	4	8.61	73.9	26.6
31	5	10.49	67.4	15.8
46	6	7.39	75.0	27.7
70	7	6.39	75.1	28.5
93	8	6.08	73.6	23.0
144	9	5.21	73.6	15.8
157	10	4.40	73.9	26.2
180	11	3.06	69.6	27.1
204	12	1.32		19.5
228	13	1.32		33.3

Table 3

EXAMPLE 3

This example also illustrates the preparation of linear alkylbenzene from paraffin dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

Following the procedures of Example 2, the alkylation unit was charged with 250 cc of the HF-treated mordenite of Example B, and the liquid feed comprised a benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 5:1 molar ratio of benzene/C₁₀-C₁₄ olefin, the reboiler temperature was typically in the range of 122-188°C, the column head temperature 78-83°C. Typical analytical results are summarized in Table 4.

After 503 hours on stream, the recovered HF-treated mordenite catalyst showed on analysis: F: 1.0%; Acidity: 0.35 meq/g; H₂O: 0.1%

Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)	Corrected ^a Alkylate Conc. (%)
0	0	1.0		8.9	1.1
2	1	3.5	61.8	0.3	3.5
4	2	7.1	72.1	0	7.1
6	3	6.8	76.7	7.2	7.3
34	4	8.4	79.7	14.3	9.8
71	5	7.2	81.8	14.6	8.5
96	6	6.5	80.8	15.5	7.7
119	7	6.3	80.6	15.1	7.4
643	8	6.0	81.0	14.3	7.0
168	9	5.9	80.7	14.4	6.9
239	10	5.0	78.2	8.8	5.5
263	11	5.3	79.2	13.5	6.2
288	12	5.0	79.6	16.5	6.0
311	13	5.4	79.4	4.1	5.6
335	14	5.5	79.2	8.2	6.0
408	15	4.9	79.4	13.1	5.6
432	16	4.7	78.8	14.4	5.5
456	17	4.4	78.5	14.1	5.1
479	18 ^a	4.7	78.6	2.7 ^b	4.8
488	19 ^b	4.9	78.5	2.4 ^c	5.0
503	20 ^b	5.1	78.9	0.6 ^c	5.1

Table 4

^a Corrected for benzene in effluent sample.^b Applied pressure 8" H₂O^c Applied pressure 12" H₂O

Example 4

This example also illustrates the preparation of linear alkylbenzenes from paraffin dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

Following the procedures of Example 2, alkylation was conducted in the glassware unit of FIG. 1 complete with catalyst column, reboiler, condenser and controls. To the reaction zone was charged 500 cc of HF-treated mordenite of Example B. The liquid feed comprised a benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 5:1 molar ratio of benzene /C₁₀-C₁₄ olefin. The feed rate was 100 cc/hr (LHSV:0.2 hr⁻¹).

Under typical steady state, reflux, conditions, with a reboiler temperature range of 131-205°C and a head temperature of 76-83°C, typical results are summarized in Table 5.

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Pressure (Inch H ₂ O)	Reboiler Temp. (C)	Time on Stream (Hrs)	Sample	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)	Corrected ^a Alkylate Conc. (%)
12	205	2	1	8.2	74.3	0.5	8.3
	193	4	2	9.2	75.0	0.4	9.2
	175	6	3	10.0	74.8	2.3	10.3
	204	21	4	12.7	78.7	0.3	12.7
	146	44	5	11.7	81.0	10.4	12.9
	136	68	6	11.5	81.8	10.0	12.7
		2-3 days	C ^b	11.6	81.4	9.4	12.7
	136	93	7	11.3	82.6	10.8	12.5
		4-5 days	C-1 ^b	11.0	81.8	11.0	12.2
	142	165	8	10.4	83.0	11.4	11.5
	142	189	9	10.2	83.4	10.5	11.2
	146	213	10	9.7	80.2	11.2	10.7
	139	238	11	9.6	83.4	11.1	10.7
	143	261	12	9.9	81.9	11.0	11.0
	133	333	13	9.2	83.4	11.3	10.3
	138	356	14	8.9	83.5	11.1	9.9
	138	381	15	8.8	83.0	11.3	9.8
	131	405	16	8.7	82.8	11.2	9.7

Table 5

^a Corrected for benzene in effluent sample

^b Composite product

EXAMPLE 5

This example illustrates the preparation of linear alkylbenzenes from paraffin dehydrogenate using a hydrogen fluoride-treated mordenite catalyst.

Following the procedures of Example 2, alkylation of benzene with C₁₀-C₁₄ paraffin dehydrogenate was conducted using the stainless-steel unit of FIG. 2, complete with catalyst column, reboiler, condenser, and controls. About 250 cc of HF-treated mordenite of Example B was charged to the column. The liquid feed comprised benzene plus C₁₀-C₁₄ paraffin dehydrogenate mix in a 10:1 molar ratio of benzene/C₁₀-C₁₄ olefin. The LHSV varied from 0.2 to 0.4 hr⁻¹.

Alkylation was conducted over a range of column and reboiler temperatures and a range of exit pressures. Typical results are summarized in Table 6.

Column Temp (°C)	Pressure DIFF EXIT (psi) (psi)		Pot Temp. (°C)	Time (hr)	Sample (#)	Alkylate Conc. (%)	2-Phenyl Sel. (%)	C ₆ H ₆ Conc. (%)
149-129	0.1	0	188	4	1	3.8		6.3
152-126	0	0	200	20	2	1.8		32.7
195-108	0	0	199	25	3	5.7		8.7
218-111	0	0	201	28	4	0.8		67.5
212-118	0	0	201	44	5	8.8	71.7	4.5
209-114	0.2	0	198	52	6	2.4		47.3
228-116	0	0	197	68	7	6.9	72.6	12.4
187-107	0.5	0	197	76	8	2.9	74.6	44.1
				76	9 ^a	4.8	72.9	25.3
					9C ^b	6.8	72.2	1.0
174-107	0	0	178	6	10	4.1	79.2	54.9
170-106	0	0	172	22	11	2.0		59.8
				28	12 ^a	6.6	76.8	26.8
142-107	0	0	136	31	13	4.8	67.9	18.9
141-110	0	0	138	47	14	4.4	65.9	16.9
142-110	0	0	136	55	15	5.0	63.9	16.6
168-111	0	0	131	71	16	4.1	64.8	16.7
170-108	0	0	150	79	17	5.0	72.0	8.8
175-113	0	0	143	95	18	5.9	68.1	15.2
145-106	0	5.2	188	14	19	3.2	60.2	9.0
149-108	0	4.2	186	20	20	4.8	66.3	12.0
160-118	0	11.7	213	29	21	4.2		6.7
160-119	0	9.3	210	44	22	5.2		6.6

Table 6

^a Composite product

^b Stripped composite product

EXAMPLES 6-8

These examples illustrate the preparation of linear alkylbenzene using hydrogen fluoride-modified mordenite catalysts with different fluoride treatment levels.

Following the procedures of Example 1, the alkylation unit was charged with benzene (100 ml), a 10 g sample of hydrogen fluoride-modified mordenite prepared by the procedure of Example B, plus a mix of benzene (50 ml) and 1-decene (10 g). Three HF-treated mordenites were tested, having the composition:

Catalyst "C" 0.25% HF on mordenite (CBV-20A)

Catalyst "D" 0.50% HF on mordenite (CBV-20A)

Catalyst "E" 1.0% HF on mordenite (CBV-20A)

In each experiment samples of the bottoms liquid fraction were withdrawn at regular periods and subject to gas chromatography analyses. The results are summarized in Table 7.

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CATALYST	TIME	%LLAB	%ISOS	%HVY	%2Ph	%3Ph	%4Ph	%5Ph	%6&7Ph
D	10	11.75	0.14	0	73.36	21.87	2.89	0.94	1.02
	20	12.43	0.21	0	72.97	21.96	3.14	1.13	0.81
	30	12.88	0.21	0	72.67	22.13	3.03	1.16	1.01
	40	12.27	0.22	0	73.02	21.92	2.85	1.06	1.14
	50	12.15	0.98	0	72.46	21.67	3.21	1.17	1.49
	50	12.24	1.01	0	72.53	21.63	3.23	1.12	1.44
	60	12.28	0.21	0	72.96	22.07	2.93	1.14	0.91
	60	11.98	0.21	0	72.97	22.21	2.93	1.17	0.83
C	10	12.2	0.18	0	72.54	22.46	3.21	0.98	0.82
	20	12.7	0.39	0	71.51	22.61	2.91	1.02	2.13
	30	12.52	0.21	0	71.96	22.68	2.96	1.04	1.36
	40	12.75	0.21	0	71.84	22.67	3.22	1.02	1.25
	50	12.98	0.21	0	71.57	22.81	3.16	1.08	1.39
	60	12.54	0.21	0	71.45	22.81	3.19	1.12	1.44
	60	12.33	0.21	0	71.61	22.87	2.92	1.05	1.31
E	10	10.56	0.05	0	75.19	19.41	2.18	3.22	
	20	12.95	0.15	0	74.36	19.23	3.01	3.4	
	30	13.44	0.18	0	74.11	19.42	3.2	3.27	
	40	13.16	0.15	0	74.16	19.38	3.12	3.34	
	50	13.1	0.15	0	74.43	19.16	3.21	3.28	
	60	12.83	0.15	0	74.28	19.49	2.88	3.35	
	60	12.87	0.16	0	73.82	19.97	2.8	3.2	

Table 7

Example 9

This example illustrates the inactivity of a heavily loaded hydrogen-fluoride modified mordenite catalyst.

Following the procedures of Example 2, the alkylation unit was charged with 100 cc of a hydrogen fluoride-treated mordenite (CBV-20A) prepared by the method of Example B but having a much higher loading of HF (fluoride content 4.8%). The acidity of said HF-treated mordenite was 0.15 meq/g.

No significant amount of alkylated product was detected by gas chromatography.

EXAMPLE 10

Preparation of high 2-position isomer C12-alkyltoluene

C12-Linear alkyltoluene (LAT) is prepared by using mordenite, CBV20A, a mordenite catalyst available from Zeolyst, Inc. of Conshohocken, Pennsylvania. The reaction was conducted in a 2L round-bottom flask equipped with a mechanical stirrer, condenser, and a Dean-Stark trap to remove water from the reaction mixture. About 50 grams of freshly calcined (1000° F) CBV20A mixed with 920 grams of reagent grade toluene and stirred under moderate agitation, with heating to reflux. About 25 ml of cloudy toluene is collected into the trap and is removed from the trap to make the reaction anhydrous. About 168 grams of alpha dodecene is added slowly over 15 minutes and continued stirring for about one hour at 130-135°C. The reaction mixture was cooled, filtered, and the excess toluene is distilled off obtain the crude alkyltoluene. The crude material is distilled under vacuo at 150-155°C at 1-2 mm pressure. Gas chromatography analysis showed a mixture of 2-tolyl isomer (84.20%), 3-tolyl isomer (15.77%) consisting of ortho, para, and meta isomers, with the para isomer being predominant.

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EXAMPLE 11

Preparation of high 2-position isomer C10-alkyltoluene

C10-linear alkyltoluene (LAT) is prepared by using mordenite, CBV20A, catalyst with/without fluoride. The reaction apparatus is the same as the one used in Example 10 above. About 50 grams of freshly calcined (1000° F) catalyst is stirred with 500 grams of reagent grade toluene and heated to reflux with moderate mechanical stirring. About 25 ml of toluene is collected into the trap to make the reaction mixture anhydrous. About 140 grams of C10-alpha olefin is added over 15 minutes and heated with stirring at 120-130°C for 30 mints., cooled and filtered. Excess toluene is removed by distillation, and the crude alkyltoluene is distilled under vacuo at 145-150°C at 1-2 mm. Gas chromatography analysis of the distilled fraction showed a mixture of 2-tolyl isomer (84.04%), 3-tolyl isomer (15 .78%), each containing para/ortho/meta isomers, with predominant isomers being the para isomers.

Example 12

Preparation of high 2-position isomer Light alkyltoluenes

Linear light alkyltoluene (LLAT) is prepared by using mordenite CBV20A catalyst. The reactor setup is the same as for Example 10 above. About 50 grams of freshly calcined (1000°F) CBV20A is mixed with 400 grams of reagent grade toluene and heated to reflux with moderate mechanical stirring at 120-125°C. About 25 ml of toluene azeotrope is removed to make the reaction completely anhydrous. About 600 grams of a hydrocarbon mix containing about 10% olefins and 90 % paraffins is added slowly over 30 minutes, and heating continued for about 2 hours at 130-135°C. The reaction mixture is cooled, filtered, and the excess toluene is removed to obtain a

crude alkyltoluene / paraffin mixture. Paraffin is removed by distillation up to 250°C. The final product is distilled at 145-155C at 1-2mm pressure. Gas chromatography analysis of distilled product showed a mixture of C10-C13 alkyltoluenes, with only 2 and 3 phenyl isomers containing para/ortho/meta isomers.

Compositions Having Enhanced Water Hardness Tolerance

A surprising observation of increased water hardness tolerance was unexpectedly observed when using LAB sulfonates having a high 2-phenyl isomer content in various cleaning formulations, as set forth below. As is well-known to those of ordinary skill in the chemical arts, most ordinary "tap" water contains varying amounts of cations of the alkaline earth metals calcium and magnesium. These metals are well known to form relatively insoluble complexes (a.k.a. "soap scum") with most soap and detergent molecules, including the LAB sulfonate materials of the prior art. Such complexation frequently results in precipitation of the salts formed by the union of the above-mentioned cations with materials commonly used as soaps, and such complexation results in precipitation of the complex with an attendant effective decrease of the total concentration of detergent in solution. This is an especially troubling problem in areas such as parts of Texas where the local water supply may contain as much as 0.10 % of calcium and magnesium hardness, which render some soaps and detergents essentially useless. To reduce the effects of hardness, formulators must often add a chelating agent such as borax, zeolites, citric acid, or EDTA or one of its sodium salts, to form stable, soluble complexes with hardness minerals, thus masking and effectively reducing the effective concentration of the hardness minerals.

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It was unexpectedly discovered that ionic metallic species such as alkaline earth metal cations which normally hinder detergent activity by complexation as described above do not form insoluble complexes with the LAB sulfonates having a high 2-phenyl isomer content as provided herein as readily as they do with LAB sulfonates in formulations provided by a prior art. The net result of the reluctance of such ionic metallic species to form insoluble complexes with LAB sulfonates having a high-2-phenyl isomer provided by the invention and the formulations described herein is that an effectively higher concentration of such active detergent components is present in solution and available for solubilization of oils and general cleaning of exposed substrates. This result is astounding, since hardness minerals have forever been an issue in the formulation of every detergent and cleaning composition because of their propensity to form insoluble salts with surface active agents. Thus, the formulations of this invention are pioneering inasmuch as they represent a first major step away from considering alkaline earth cations as being an issue in the formulation of detergents and the like.

However, the LAB sulfonates of this invention which have a higher 2-phenyl isomer content than were previously available from the teachings of the prior art also have a Krafft temperature which is in the range of between about 15°C to 30° C, depending upon the length of the alkyl chain. In cases where such high Krafft temperatures are undesirable, these LAB's may not be the material of choice, all things considered. However, the LAT sulfonates of this invention which have a 2-phenyl isomer content in the range of between about 30.00% and 80.00 % have been observed to have much lower Krafft temperatures, typically less than 10° C, and more typically in the range of between -5°C and +5° C. These lower Krafft temperatures are beneficial in

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providing the micellular structures necessary for acceptable detergency characteristics in most applications; however, the water hardness tolerance of the high 2-toluyll isomer LAT materials is particularly dependent upon the alkyl chain length in the LAT materials. As is evident from FIG. 10, when the average alkyl chain length of the LAT material is below about 10.8, the water hardness tolerance is superior to LAB material. However, when the average alkyl chain length is greater than about 11, then the water hardness tolerance is inferior to LAB material. Thus it has been found beneficial in some formulations to employ mixtures of the high 2-phenyl isomer LAT materials and high 2-phenyl isomer LAB materials, in order to arrive at a component useful in detergent formulations which has enhanced detergency characteristics at lower temperatures and a high degree of water hardness tolerance.

Through use of the components having a high 2-phenyl isomer content as provided herein, formulators may in many instances omit a chelating agent from their formulations, or at the least, only moderate, reduced amounts would be required. Since such chelants are relatively costly, a savings in manufacture from the standpoints of blending and raw material quantities may be passed on to the public.

Cleaning compositions which utilize an alkylbenzene sulfonate of this invention having a 2-phenyl isomer content of about 80% in the stead of those having a 2-phenyl isomer content of less than about 50% are in general are possessive of much greater cleaning strength. The increase in cleaning performance provided by the linear alkylbenzene sulfonates of this invention having a 2-phenyl isomer content of about 80% ("Super High 2-Phenyl") is illustrated by the data set forth in **FIG. 5** below. In **FIG. 5**, the total detergency of a blend comprising a conventional linear alkylbenzene sulfonate (denoted as A225 that comprises a 2-phenyl isomer content of about 16 % to

18% of the total alkylbenzene sulfonates present; A225 is available from Huntsman Petrochemical Corporation located at 7114 North Lamar Blvd., Austin, Texas.) containing various added amounts of Super High 2-Phenyl is illustrated as performance from laundry testing data. For this series of tests, Super High 2-Phenyl was blended with A225 holding the total amount of actives constant at 10%. The samples were tested in a 6 pot Terg-o-tometer® (US Testing Corporation) at 2 grams per liter of detergent at 100 degrees Fahrenheit, using a 150 ppm hard water with a 15 minute wash cycle followed by a 5 minute rinse. Standardized soil swatches were used to assess the detergency. Results were obtained by measuring the reflectance of the swatches both before and after cleaning using a Hunter Lab Color Quest reflectometer using the L-A-B scale. All swatches were run in triplicate and the results averaged. Soil swatches used were: dirty motor oil, dust sebum, grass stain, blood/milk/ink stain, olive oil (EMPA), clay, and clean white swatches to measure redeposition. Both cotton and polyester/cotton blends were evaluated for all soils. The results show that the cleaning performance increases with increasing percentage of 2-phenyl isomer content in the blend. The results for the detergent which employed 100 % of material containing a high 2-phenyl isomer content were as much as 50 % higher than the conventional linear alkylbenzene sulfonate ("LAS"). In all solutions employed herein for hardness testing, a calcium to magnesium ratio of 2 to 1 was employed.

As mentioned above, detergents formulated using Super High 2-Phenyl exhibit an increased tolerance to water hardness with respect to those formulated using conventional, commercially-available linear alkyl benzene sulfonate detergent components. **FIG. 6** below provides turbidity data to evidence the hardness tolerance of conventional LAS surfactant A225 present at about 1 % aqueous at various levels of

water hardness, as measured in NTU units (using a turbidimeter from Orbeco-Helige of Farmingdale, NY), the use of which is well known to those of ordinary skill in the art. In **FIG. 6**, the point at which the solution turbidity first undergoes a dramatic increase is the point approximately corresponding to the solubility limit of the complex formed by the hardness minerals found in the water used and the detergent component. Thus, formulations which employ conventional linear alkylbenzene sulfonate components similar to A225 begin to experience a decrease in the effective concentration of a main ingredient at a water hardness level of around 750 ppm. Of course such effect will be more pronounced for consumers wishing to ration detergents by using less soap in a given volume of water than the recommended amount, since the amount of total hardness with respect to available sulfonate will be greatly increased which may in some cases bind up more than half of the sulfonate present.

FIG. 7 provides data for the same hardness tolerance data as was gathered for **FIG. 6** present at about 1 % aqueous; however, the LAS used for gathering these data was the Super High 2-Phenyl LAS. From the data in **FIG. 7**, it is evident that significant amounts of water-insoluble compounds are not formed until a hardness level of about 1500 ppm is reached, which is about twice the hardness tolerance of conventional materials. Since the formulations according to the invention contain high amounts of the 2-phenyl isomer of linear alkylbenzene sulfonates, they not only have increased detergency power, but are also more tolerant to water hardness. Thus, less active chemical may be used in a formulation to give it equal cleaning power to prior art formulations which contain greater amounts of linear alkylbenzene sulfonates. Lowering the amount of active chemical in the formulation saves in raw material costs,

blending operations, and transportation costs, which savings may be passed on to the public.

FIG. 8 provides data for the same hardness tolerance data as was gathered for **FIGS. 6** and **7**; however the surfactant concentration was reduced to about 0.1 % aqueous to show the effect of reduced surfactant concentration, since the point at which precipitates begin to form is dependent upon the total amount of surfactant present. In **FIG. 8**, both A225 and an alkylbenzene sulfonate provided according to the invention having a 2-phenyl isomer are compared. From these data, it is evident that significant amounts of water-insoluble compounds are formed at hardness levels of about 25 ppm using the conventional A225 material while the Super High 2-phenyl material does not show any precipitation until the hardness level of four time this amount or about 100 ppm is achieved.

FIG. 9 illustrates an unexpected synergy discovered with respect to blends containing linear alkylbenzene sulfonates and linear alkyltoluene sulfonates, in which both of these sulfonated aromatic alkylates have a 2-phenyl isomer content greater than 75%. The data on the graph are NTU turbidity values for a 0.10% aqueous solution (hardness of 300 ppm, Ca/Mg = 2:1) to which blends containing these linear alkylbenzene sulfonates (SLAS) and linear alkyltoluene sulfonates (SLATS) are present in varying amounts. For each data point, the total combined amount of surfactant is the same at 0.10 % of the total solution. From the graph can be observed the unexpected minimum when the amount of alkyltoluene sulfonates present are between about 15% and 55% of the total amount of surfactant present.

Since such a large number of formulations of various cleaning compositions contain linear alkylbenzene sulfonates as a main detergent component, the breadth of

applicability of the discoveries according to this invention is great indeed. Thus, all cleaning compositions known in the prior art which contain sulfonated linear alkylbenzenes can be increased in effectiveness and cleaning strength by being reformulated to replace at least a portion of the sulfonated linear alkylbenzenes currently used with a sulfonated linear alkyltoluene surfactant provided by this invention that have an increased percentage of 2-phenyl alkyltoluene isomers over what was previously available. Further, since it is possible to blend an LAT sulfonate having a high 2-phenyl isomer content produced in accordance with the present invention (on the order of about 82 %) with conventional LAB or LAT sulfonates, it is also possible according to the invention to provide a mixed LAB/LAT sulfonate component useful for forming a detergent composition or cleaning formulation in which the component has a 2-phenyl isomer content of any selected value between about 18% and 82 % by weight based upon the total combined weight of all isomers of LAB and LAT sulfonates present. As shown in Table 5, alkylbenzenes that contain amounts of the 2-phenyl isomer in excess of 80% may be readily produced according to the instant process using the instant catalyst.

Formulators of finished detergents would prefer to use LAB based surfactants having a 2-phenyl isomer content in the range from about 30 to 40 percent, but this level has not heretofore been available in commercial quantities. Through use of the instant invention, a wide variety of cleaning products comprising LAB and LAT sulfonates having between 30% and 40% of 2-phenyl isomer are easily achieved for the first time on a commercial scale. Below are set forth examples of some superior formulations which employ sulfonated linear alkylbenzenes as surfactants. In each example, the LAB sulfonate and the LAT sulfonate used are sulfonates produced in accordance

with table 2, and having 2-phenyl isomer contents of about 81 %. In the examples, the term "LAB sulfonate having 80% 2-phenyl content" means an LAB sulfonate having a 2-phenyl isomer content of 80 % based upon the total of all LAB sulfonate isomers present in the LAB sulfonate. The term "LAT sulfonate having 80% 2-phenyl content" means an LAT sulfonate having a 2-phenyl isomer content of 80 % based upon the total of all LAT sulfonate isomers present in the LAT sulfonate. In each of the Examples given below, all of the ingredients were combined with one another and mixed until homogeneous. Then, in each case, the final mixtures were adjusted , as is done according to a preferred form of the invention, to a pH in the range of 10-11 using aqueous NaOH and HCl, as needed. However, any final pH level in the range of about 7 – 12 is may be achieved. In liquid dishwashing liquids, a pH in the range of about 7-8 is most desirable.

It will be seen in the examples below that there are components in each of the formulas other than the alkylbenzene surfactant component having a high 2-phenyl isomer content. These other components are known by those of ordinary skill in this art to be useful in formulating soaps, cleaning compositions, hard surface cleaners, laundry detergents, and the like. For purposes of this invention and the appended claims, the words "other components known to be useful in formulating soaps, detergents, and the like" means any material which a formulator of ordinary skill in the soap or detergent arts recognizes as adding a benefit to the physical performance, aroma, or aesthetics of a combination that is intended to be used as a cleaning composition, regardless of the substrate that is intended to be cleansed. Such includes every material that has been known in the prior art to be useful in soap and detergent formulations.

In each of the Examples which follow, all percentages are given on a percent by weight basis based on the total weight of the finished composition, unless noted otherwise.

Example 13 - All Purpose Cleaner

LAT sulfonate having 80% 2-phenyl content	1.3
LAB sulfonate having 80% 2-phenyl content	2.0
alkyl sulfate	1.6
coconut fatty acid	1.8
monoethanolamine	1.5
SURFONIC® L12-6	12.4
Amine oxide	0.9
Soda ash	0.7
Water	77.8
Total	100

Example 14 - All Purpose Cleaner

LAT sulfonate having 80% 2-phenyl content	0.66
LAB sulfonate having 80% 2-phenyl content	2.64
alkyl sulfate	1.6
coconut fatty acid	1.8
monoethanolamine	1.5
SURFONIC® L12-6	12.4
Amine oxide	0.9
Soda ash	0.7
Water	77.8
Total	100

Example 15 - All Purpose Cleaner

LAT sulfonate having 80% 2-phenyl content	0.66
LAB sulfonate having 2-phenyl content between 12.0 % and 30.0%	2.64
alkyl sulfate	1.6
coconut fatty acid	1.8
monoethanolamine	1.5
SURFONIC® L12-6	12.4
Amine oxide	0.9
Soda ash	0.7
Water	77.8
Total	100

Example 16 - Pine Oil Microemulsion

Pine Oil	20.0
SURFONIC® L12-8	4.7
LAT sulfonate having 80% 2-phenyl content	3.12
LAB sulfonate having 80% 2-phenyl content	4.68
Isopropanol	11.0
Triethanolamine	4.7
Water	51.8
Total	100

Example 17 - Pine Oil Microemulsion

Pine Oil	20.0
SURFONIC® L12-8	4.7
LAT sulfonate having 80% 2-phenyl content	1.56
LAB sulfonate having 80% 2-phenyl content	6.24
Isopropanol	11.0
Triethanolamine	4.7
Water	51.8
Total	100

Example 18 - Pine Oil Microemulsion

Pine Oil	20.0
SURFONIC® L12-8	4.7
LAT sulfonate having 80% 2-phenyl content	1.56
LAB sulfonate having 2-phenyl content between 12.0% and 30.0%	6.24
Isopropanol	11.0
Triethanolamine	4.7
Water	51.8
Total	100

Example 19 - Value Brand Powdered Laundry Detergent

LAB sulfonate having 80% 2-phenyl content	3.9
LAT sulfonate having 80% 2-phenyl content	2.6
SURFONIC® N-95	4.3
Soda ash	29.8
Sodium chloride	45.7
Sodium silicate	11.6

Polymer	2.1
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Example 20 - Value Brand Powdered Laundry Detergent

LAB sulfonate having 80 %2-phenyl content	5.2
LAT sulfonate having 80% 2-phenyl content	1.3
SURFONIC® N-95	4.3
Soda ash	29.8
Sodium chloride	45.7
Sodium silicate	11.6
Polymer	2.1

Example 21 - Value Brand Powdered Laundry Detergent

LAB sulfonate having 2-phenyl content between 12.0% and 30.0%	3.9
LAT sulfonate having 80% 2-phenyl content	2.6
SURFONIC® N-95	4.3
Soda ash	29.8
Sodium chloride	45.7
Sodium silicate	11.6
Polymer	2.1

Example 22 - Premium Brand Powdered Laundry Detergent

LAB sulfonate having 80% 2-phenyl content	5.68
LAT sulfonate having 80% 2-phenyl content	1.42
Sodium alkyl sulfate	13.3
Alcohol ethoxylate	2.6
Zeolites	34.7
Soda ash	19.6
Sodium silicate	1.0
Sodium perborate	0.9
TAED	0.5
Sodium sulfate	19.3
Protease enzyme	0.5
Cellulase enzyme	0.5
Total	100

Example 23 - Premium Brand Powdered Laundry Detergent

LAB sulfonate having 80% 2-phenyl content	4.26
LAT sulfonate having 80% 2-phenyl content	2.84
Sodium alkyl sulfate	13.3
Alcohol ethoxylate	2.6
Zeolites	34.7
Soda ash	19.6
Sodium silicate	1.0
Sodium perborate	0.9
TAED	0.5
Sodium sulfate	19.3
Protease enzyme	0.5
Cellulase enzyme	0.5
Total	100

Example 24 - Premium Brand Powdered Laundry Detergent

LAB sulfonate having 2-phenyl content between 12.0% and 30.0%	4.26
LAT sulfonate having 80% 2-phenyl content	2.84
Sodium alkyl sulfate	13.3
Alcohol ethoxylate	2.6
Zeolites	34.7
Soda ash	19.6
Sodium silicate	1.0
Sodium perborate	0.9
TAED	0.5
Sodium sulfate	19.3
Protease enzyme	0.5
Cellulase enzyme	0.5
Total	100

Example 25 - Value Brand Laundry Concentrate

LAB sulfonate having 80% 2-phenyl content	11.1
LAT sulfonate having 80% 2-phenyl content	7.4
SURFONIC® N-95	75.00

Monoethanolamine	6.50
Total	100

Example 26 - Value Brand Laundry Concentrate

LAB sulfonate having 80% 2-phenyl content	14.8
LAT sulfonate having 80% 2-phenyl content	3.7
SURFONIC® N-95	75.00
Monoethanolamine	6.50
Total	100

Example 27 - Value Brand Laundry Concentrate

LAB sulfonate having 2-phenyl content between 12.0% and 30.0%	14.8
LAT sulfonate having 80% 2-phenyl content	3.7
SURFONIC® N-95	75.00
Monoethanolamine	6.50
Total	100

Example 28 - Value Brand Laundry Detergent

Concentrate from Example 22, 23, or 24	7.0000
Water (well)	92.168
Optical Brightener	0.0100
Salt	0.1352
Salt	0.6148
Preservative	0.0100
Dye	0.0020
Fragrance	0.0600
Total	100

Example 29 - Value Brand Laundry Concentrate

LAB sulfonate having 80% 2-phenyl content	10.44
LAT sulfonate having 80% 2-phenyl content	7.00
SURFONIC® N-95	34.8
SURFONIC® T-15	17.4
POGOL® 300	8.0
Monoethanolamine	2.4
Water	20.0
Total	100

Example 30 - Value Brand Laundry Concentrate

LAB sulfonate having 80% 2-phenyl content	13.92
LAT sulfonate having 80% 2-phenyl content	3.48
SURFONIC® N-95	34.8
SURFONIC® T-15	17.4
POGOL® 300	8.0
Monoethanolamine	2.4
Water	20.0
Total	100

Example 31 - Value Brand Laundry Concentrate

LAB sulfonate having 2-phenyl content between 12.0% and 30.0%	13.92
LAT sulfonate having 80% 2-phenyl content	3.48
SURFONIC® N-95	34.8
SURFONIC® T-15	17.4
POGOL® 300	8.0
Monoethanolamine	2.4
Water	20.0
Total	100

Example 32 - Value Brand Laundry Detergent

Concentrate from Example 26, 27, or 28	50.000
Water	44.245
Optical brightener A	0.15
Sodium chloride	0.500
Polyacrylate A	2.500
Chelating agent	1.00
NaOH (50.0% aq.)	0.220
Fragrance	0.300
Preservative	0.080
Melaleuca oil	0.005
Total	100

Example 33 - Premium Laundry Detergent with Enzymes

Concentrate from Example 30, 31, or 32	30.0000
Water (well)	56.2632
Optical brightener	0.0500
Calcium dichloride	0.1000
Sodium chloride	0.6148
Preservative	0.0100
Dye	0.0020
Fragrance	0.0600
Propylene glycol	10.0000
Borax	2.0000
Protease enzyme	0.7000
Lipase enzyme	0.2000
Total	100

Example 34 - Premium Liquid Dishwashing Formulation I

LAB sulfonate having 80% 2-phenyl content	15.44
LAT sulfonate having 80% 2-phenyl content	10.31
De-ionized water	16.316
Magnesium hydroxide	1.133
Sodium hydroxide (38% aq.)	3.591
SURFONIC® SXS-40 (40% aq.)	15.000
Propylene glycol	6.000
Sodium lauryl ether sulfate (3 moles EO, 70 % aq.)	14.286 (molecular weight = 440)
Cocoamidopropyl betaine (38 % aq.)	15.789
Ethanol	0.0300
Tetrasodium EDTA	0.1500
Preservative	0.2000
Dye (0.8% aq.)	1.0000
Fragrance	0.5000
Total	100

Example 35 - Premium Liquid Dishwashing Formulation

LAB sulfonate having 80% 2-phenyl content	20.59
LAT sulfonate having 80% 2-phenyl content	5.16
De-ionized water	16.316
Magnesium hydroxide	1.133
Sodium hydroxide (38% aq.)	3.591
SURFONIC® SXS-40 (40% aq.)	15.000
Propylene glycol	6.000
Sodium lauryl ether sulfate(3 moles EO, 70 % aq.)	14.286 (molecular weight = 440)
Cocoamidopropyl betaine (38 % aq.)	15.789
Ethanol	0.0300
Tetrasodium EDTA	0.1500
Preservative	0.2000
Dye (0.8% aq.)	1.0000
Fragrance	0.5000
Total	100

Example 36 - Premium Liquid Dishwashing Formulation

LAB sulfonate having 2-phenyl content between 12.0% and 30.0%	20.59
LAT sulfonate having 80% 2-phenyl content	5.16
De-ionized water	16.316
Magnesium hydroxide	1.133
Sodium hydroxide (38% aq.)	3.591
SURFONIC® SXS-40 (40% aq.)	15.000
Propylene glycol	6.000
Sodium lauryl ether sulfate (3 moles EO, 70 % aq.)	14.286 (mw =440)
Cocoamidopropyl betaine (38 % aq.)	15.789
Ethanol	0.0300
Tetrasodium EDTA	0.1500
Preservative	0.2000
Dye (0.8% aq.)	1.0000
Fragrance	0.5000
Total	100

Example 37 - Premium Liquid Dishwashing Formulation

LAB sulfonate having 80% 2-phenyl content	6.12
LAT sulfonate having 80% 2-phenyl content	4.08
De-ionized water	35.567
Magnesium hydroxide	1.133
Sodium hydroxide (38 % aq.)	1.250
SURFONIC® SXS-40 (40% aq.)	15.000
Propylene glycol	6.000
Sodium lauryl ether sulfate (40% aq.)	20.000 (molecular weight = 440)
Alkyl polyglycoside (50% aq.)	6.000
Fatty acid MEA amide	3.000
Tetrasodium EDTA	0.150
Preservative	0.200
Fragrance	0.500
Total	100

Example 38 - Premium Liquid Dishwashing Formulation

LAB sulfonate having 80% 2-phenyl content	8.16
LAT sulfonate having 80% 2-phenyl content	2.04
De-ionized water	35.567
Magnesium hydroxide	1.133
Sodium hydroxide (38 % aq.)	1.250
SURFONIC® SXS-40 (40% aq.)	15.000
Propylene glycol	6.000
Sodium lauryl ether sulfate (40% aq.)	20.000 (molecular weight = 440)
Alkyl polyglycoside (50% aq.)	6.000
Fatty acid MEA amide	3.000
Tetrasodium EDTA	0.150
Preservative	0.200
Fragrance	0.500
Total	100

Example 39 - Premium Liquid Dishwashing Formulation

LAB sulfonate having 2-phenyl content between 12.0% and 30.0%	8.16
LAT sulfonate having 80% 2-phenyl content	2.04
De-ionized water	35.567
Magnesium hydroxide	1.133
Sodium hydroxide (38 % aq.)	1.250
SURFONIC® SXS-40 (40% aq.)	15.000
Propylene glycol	6.000
Sodium lauryl ether sulfate (40% aq.)	20.000 (molecular weight = 440)
Alkyl polyglycoside (50% aq.)	6.000
Fatty acid MEA amide	3.000
Tetrasodium EDTA	0.150
Preservative	0.200
Fragrance	0.500
Total	100

Example 40 - Powdered Aircraft Cleaner

Metso pentabead 20 (sodium metasilicate)	30.0
Sodium tripolyphosphate	30.0
Ammonium bifluoride	8.0
Tetrasodium pyrophosphate	20.0
LAB sulfonate having 80% 2-phenyl content	4.0
LAT sulfonate having 80% 2-phenyl content	8.0

Example 41 - Powdered Aircraft Cleaner

Metso pentabead 20 (sodium metasilicate)	30.0
Sodium tripolyphosphate	30.0
Ammonium bifluoride	8.0
Tetrasodium pyrophosphate	20.0
LAB sulfonate having 80% 2-phenyl content	8.0
LAT sulfonate having 80% 2-phenyl content	4.0

Example 42 - Powdered Aircraft Cleaner

Metso pentabead 20 (sodium metasilicate)	30.0
Sodium tripolyphosphate	30.0
Ammonium bifluoride	8.0
Tetrasodium pyrophosphate	20.0
LAB sulfonate having 80% 2-phenyl content	8.0
LAT sulfonate having 80% 2-phenyl content	4.0

Example 43 - Dairy Cleaner

Sodium hexametaphosphate	20.00
Sodium Sulfate	20.00
LAB sulfonate having 80% 2-phenyl content	30.00
LAT sulfonate having 80% 2-phenyl content	10.00

Example 44 - Dairy Cleaner

Sodium hexametaphosphate	20.00
Sodium Sulfate	20.00
LAB sulfonate having 80% 2-phenyl content	10.00
LAT sulfonate having 80% 2-phenyl content	30.00

Example 45 - Powdered Dairy Cleaner

LAB sulfonate having 80% 2-phenyl content	3.00 - 50.00
LAT sulfonate having 80% 2-phenyl content	3.00 - 50.00
Sodium sulfate	0.00 - 20.00
Sodium metasilicate	0.00 - 30.00
Nonionic surfactant	5.00

Example 45 - Powdered Neutral Dairy Cleaner

LAB sulfonate having 80% 2-phenyl content	x (where x = 0.00 to 33.00)
LAT sulfonate having 80% 2-phenyl content	33-x

Non-ionic surfactant	1.00
Monsanto Phosphate STP/A	33.00
Monsanto Phosphate SAPP/A	33.00

Example 46 - Vehicle Wash, Powder

Sodium tripolyphosphate	36.00
Tetrasodium pyrophosphate	30.00
Sodium metasilicate, anhydrous	20.00
LAT sulfonate having 80% 2-phenyl content	5.00
Shell Chemical Co. Neodol 91-6	8.00
Monsanto Co. Dequest 2006 phosphonate	1.00

Example 47 - Aluminum Vehicle Wash, Powder

Sodium tripolyphosphate	36.00
Tetrasodium pyrophosphate	30.00
Sodium metasilicate, anhydrous	20.00
LAB sulfonate having 80% 2-phenyl content	5.00
Shell Chemical Co. Neodol 91-6	8.00
Monsanto Co. Dequest 2006 phosphonate	1.00

The above examples are intended to be exemplary of the versatility of the compositions produced according to the invention with respect to the formulation of household and commercial cleaning formulations, and are not intended to be delimitive thereof in any way whatsoever. Any formulation of a soap, detergent, cleaning composition, whether liquid or solid, regardless of its intended use, that in its common use formulation contains a LAB sulfonate as a component can be increased in effectiveness by having the current commercial LAB sulfonate component used in its formulation removed and a component comprising an LAB sulfonate component having an elevated 2-phenyl isomer content and an LAT sulfonate component having an elevated 2-phenyl isomer content substituted therefor. The present invention thus

represents a revolutionary advance in the detergent arts, since the preferred 2-phenyl isomers of aromatic alkylates may now be produced in high yield, *en masse*, for approximately the same cost as inferior prior art LAB sulfonate mixtures.

In the foregoing formulations, the relative proportions of the LAB sulfonates to the LAT sulfonates is in the range of 1.5:1 to 4:1. This is because of an unexpected synergy we have discovered in relation to the relative amounts of LAB to LAT sulfonates present in aqueous detergent solutions which contain these materials. Our discovery is depicted pictorially in **FIG. 9**.

It has also been discovered that salts of alkylbenzene sulfonates having a 2-phenyl isomer content greater than about 60 % may be isolated as solids at room temperature. This result is surprising since salts of alkylbenzene sulfonates have heretofore been believed to exist only in liquid form. Thus, by the present invention, it is now possible to provide dry powder formulations comprising alkylbenzene sulfonates, such as dry laundry detergents, dry dishwashing detergents, etc. Such dry formulations may be provided using existing blending techniques, including the use of conventional dry processing equipment such as ribbon blenders, etc., and also include detergent tablets for laundry use.

To produce a solid alkylbenzene salt according to a preferred form of the invention, one begins with the sulfonic acid mixture which is produced from sulfonating an alkylbenzene mixture prepared in accordance with the invention, such as any of samples 4 through 7 of table 2 above, which contain more than about 80.0 % of the 2-phenyl isomers. Such sulfonic acids are then dissolved in water to a concentration of about 10.0 % by weight, and neutralized by slow addition of an alkaline aqueous solution of the desired cation, such as through the use of alkali hydroxides, until

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stoichiometric neutralization has occurred, which in the case of sodium and potassium is when a pH of about 10.5 is reached. Finally, the water is removed by evaporation or by other means known to those skilled in the chemical arts, such as through the use of a ROTOVAP® evaporator or the like, spray dryer, turbodryer, etc. thus leaving crystals of the alkylbenzene sulfonate salt. Such crystals may be conveniently purified further by recrystallization from ethanol. The sodium and potassium salts of alkylbenzene sulfonate according to sample 4 of table 2 have a melting point in the range of about 50° to 80° C, depending upon the alkyl chain length, with longer chain length materials having a higher melting point. The test method used is differential scanning calorimetry according to ASTM specification D-3417.

Cationic surfactants may also function as a cation in forming a stable, solid salt of an alkylbenzene sulfonate. Cationic surfactants are well known in the art as being surfactants with a positively-charged ionic group in their molecular structure, such as the as quaternary ammonium compounds. Cationic surfactants are known to function together with other parts of a formulated detergent system to lower the water's surface tension. They are typically used in wash, rinse and dryer-added fabric softeners. Thus, when a cationic surfactant is employed for providing charge balance in a solid alkylbenzene sulfonate salt according to the invention, a formulator using such a salt is able to reap added benefit from the presence of both a cationic surfactant and an anionic surfactant in the same solid material, which may be powdered. Such salts therefore may reduce the costs associated with storage and blending of different materials, as is currently common in the art owing to the presence of both a surfactant and a detergent in the same molecule.

Owing to the unexpected finding that certain salts of the alkylbenzene sulfonates having sufficient 2-phenyl isomer content are solids at room temperature, the present invention also comprises as formulations useful for cleaning laundry which comprise solid tablets, as well as solid bars of soap comprising the solid alkylbenzene sulfonates as an active detergent component.

Detergent tablets are described, for example, in GB 911 204 (Unilever), U.S. Pat. No. 3,953,350 (Kao), JP 60 015 500A (Lion), JP 60 135 497A (Lion) and JP 60 135 498A (Lion); and are sold commercially in Spain. Detergent tablets are generally made by compressing or compacting a detergent powder, as is well-known in the art. Thus, the present invention contemplates substitution of at least a portion of, and more preferably all of, the active detergent component of a conventional laundry tablet of the prior art with a salt of an alkylbenzene sulfonate having sufficiently high 2-phenyl isomer to cause such salt to exist in the form of a solid at room temperature. Such substitution is readily made by providing such solid sulfonate in the stead of the conventional detergent component of the conventional laundry tablet during laundry tablet manufacture.

Bars of soap are made by various means known to those in the art including the pouring into molds of a caustic/oil mixture prior to its full saponification, or the use of "soap noodles" in a press with or without the aid of heat and pressure. Soaps typically include fatty acid carboxylates, perfumes, dyes, preservatives, bactericides, fillers such as talc, and other additives. The present invention contemplates substitution of at least a portion of, and more preferably all of, the active cleaning component of a conventional bar of soap of the prior art with a salt of an alkylbenzene sulfonate having sufficiently high 2-phenyl isomer to cause such salt to exist in the

form of a solid at room temperature. Such substitution is readily made by providing such solid sulfonate in the stead of the conventional detergent component of the conventional bar of soap during soap manufacture. Thus, a bar of soap according to the invention may comprise only the Super High 2-phenyl alkylbenzene sulfonate according to the invention, in combination with sufficient binders, perfumes, dyes, etc. to form a solid bar of soap, using in one form of the invention the same general compression techniques useful for producing laundry tablets.

Although the present invention has been shown and described with respect to certain preferred embodiments, it is obvious that equivalent alterations and modifications will occur to others skilled in the art upon the reading and understanding of the specification. The present invention includes all such equivalent alterations and modifications, and is limited only by the scope of the claims which now follow.

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